

UNCLASSIFIED

AD NUMBER	
AD394194	
CLASSIFICATION CHANGES	
TO:	UNCLASSIFIED
FROM:	CONFIDENTIAL
LIMITATION CHANGES	
TO: Approved for public release; distribution is unlimited.	
FROM: Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; OCT 1968. Other requests shall be referred to Air Force Rocket Propulsion Lab., Edwards AFB, CA 93523.	
AUTHORITY	
31 Oct 1980 DoDD 5200.10 ; AFRPL ltr 16 Feb 1981	

THIS PAGE IS UNCLASSIFIED

THIS REPORT HAS BEEN DELIMITED
AND CLEARED FOR PUBLIC RELEASE
UNDER DOD DIRECTIVE 5200.20 AND
NO RESTRICTIONS ARE IMPOSED UPON
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

SECURITY

MARKING

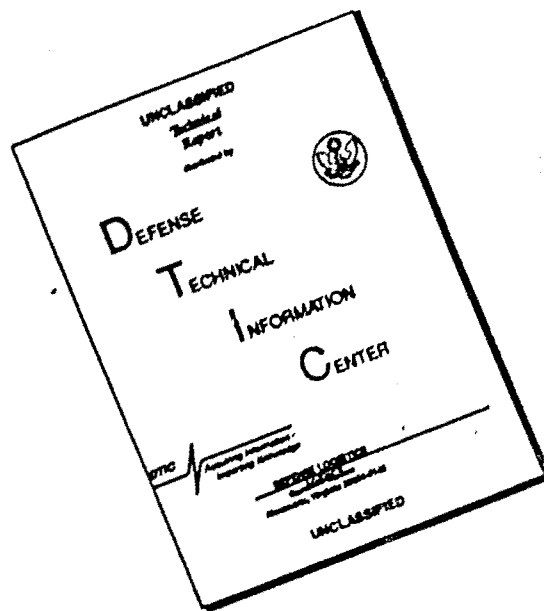
The classified or limited status of this report applies to each page, unless otherwise marked.

Separate page printouts MUST be marked accordingly.

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECTIONS 793 AND 794. THE TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U.S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

CONFIDENTIAL

This document contains information affecting the National Defense of the United States within the meaning of the Espionage Laws, Title 18 U.S.C., Sections 793 and 794. Its transmission or revelation of its contents in any manner to an unauthorized person is prohibited by law.

AFRPL-TR-68-184

Energetic Binder Production (U)

L. Hunter, E.E. Ryder, Jr.

Shell Development Company
A Division of Shell Oil Company

Sponsoring Agency:
Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards Air Force Base, California
Air Force Systems Command, United States Air Force

Final Technical Report
October 1968

Contract No. AF04(611)-11645

Project No. 3148

In addition to security requirements which must be met, this document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFRPL(RPPR-ST)NFOI, Edwards, California 93523

GROUP 4
Downgraded at 3 Year Intervals,
Declassified After 12 Years

CONFIDENTIAL

AFRPL-TR-68-184

AD 894194

DEC 12 1968

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, U.S.C. Sections 793 and 794. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

In addition to security requirements which must be met, this document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFRPL(RPPR-STINFO), Edwards, California 93523.

CONFIDENTIAL

ENERGETIC BINDER PRODUCTION (U)

Sponsoring Agency:
Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards, California
Air Force Systems Command, United States Air Force

Contract No. AF 04 (611)-11645
AFFTC Project No. 3148
BPSN 623148

FINAL TECHNICAL REPORT

October 1968

Reported: L. Hunter
E. E. Ryder

Participants: A. C. Mueller
D. D. Campbell
A. D. Fredenburg
A. J. Hilliard
J. P. Smith

Approved: K. D. Detling

Date of Issue: December 1968

In addition to security requirements which must be met, this document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFRPL(RPPR-STINFO), Edwards, California 93523.

SHELL DEVELOPMENT COMPANY
A Division of Shell Oil Company
Emeryville, California

GROUP 4
Downgraded at 3 year intervals;
declassified after 12 years

AFRPL-TR-68-184

-i-

CONFIDENTIAL

CONFIDENTIAL

FOREWORD

(U) The work described in this report was authorized under AFFTC Project No. 3148, BPSN 623148. The program was administered during the first eight months by Dr. Frank Roberto and subsequently by Capt. W. H. Anders, Air Force Rocket Propulsion Laboratory, RFCS, Edwards, California.

(C) This Final Technical Report on Contract No. AF 04(611)-11645 describes the work carried out by Shell Development Company, Emeryville, California during the period 1 March 1967 to 1 August, 1968 on the synthesis, fractionation and characterization of PBEP, the construction and development of a continuous difluoramination unit for the production of PBEP, and the supply of this material to other rocket propulsion contractors for evaluation as a high-energy binder in solid propellant systems.

(U) This report has been reviewed and is approved.

W. H. EELKE, Colonel, USAF
Chief, Propellant Division

CONFIDENTIAL

CONFIDENTIAL ABSTRACT

(C) PBEP has been fractionated by solvent gradient elution from a Chromosorb W-packed column. Molecular weight distribution of the polymer has been determined and the fractions evaluated through exhaustive analyses and small scale cure studies. PBEP has been also separated into two fractions by extraction with carbon tetrachloride. The properties of the fractions have been compared and the more promising higher molecular weight fraction extensively evaluated.

(C) Fractionation of the polymer at an earlier stage in the synthesis has been investigated. Polyepichlorohydrin (PECH) has been separated into two fractions and the higher molecular weight fraction evaluated by conversion to PBEP.

(C) The carbon treatment of PBEP has produced promising improvements in the thermal stability of the polymer and in reducing the deactivating effect of the latter on the cure catalyst.

(C) Small scale curing studies have compared the reaction of tolylene diisocyanate (TDI) with PBEP and other ingredients in the cure system. Deactivation of the cure catalyst by PBEP has been demonstrated and promising leads towards prevention have been investigated.

(U) The stability of PBEP in solution has been investigated at high and low temperatures for extended periods.

(C) Large scale batch preparations of polyepichlorohydrin (PECH) and dehydrochlorinated PECH (DEPECH) have been carried out. A two-stage continuous reactor system for difluoramination of DEPECH has been constructed and operated for the production of experimental quantities of PBEP for evaluation by propellant contractors. A brief investigation of the process variables has been carried out to determine near optimum conditions for the continuous system.

CONFIDENTIAL

CONTENTS

	Page
Summary	1
The Fractionation of PBEP	4
Introduction	4
Fractionation by Precipitation	5
Fractionation by Solution	6
Fractionation on Silica Gel	6
Fractionation on Chromosorb W	7
Fractionation by Solvent Gradient Elution	10
Evaluation of Polymer Fractions	11
Fractionation by Solvent Extraction	13
Evaluation of Raffinate Fraction	15
The Fractionation of PECH	16
Fractionation by Solvent Extraction	16
Evaluation of PECH Raffinate	17
The Fractionation of DEPECH	20
Carbon Treatment of PBEP	21
PBEP Curing Studies	22
Stability of PBEP Solutions	24
Large Scale Preparation of PECH and DEPECH	24
Addition of N ₂ F ₄ to DEPECH	24
Process Equipment Description	25
Product Quality Criteria	25
Process Variables Studied With Continuous PBEP Unit	26
Excess of N ₂ F ₄	27
Residence Time	27
Reaction Temperature	27
DEPECH Concentration	28
Pressure	28
Solvent	28
DEPECH Feed Solution Quality	28
Sample Preparation	29
Document Control Data - R and D; DD Form 1473 With Abstract and Key Word List	31

CONFIDENTIAL

LIST OF TABLES

<u>Table</u>		Page
1	Properties of PBEP (10001-186)	4
2	Properties of Precipitated PBEP Fractions	6
3	Rate of Solution of PBEP in Various Solvents	8
4	Cure Studies Using PBEP Fractions following	13
5	Comparison of Properties of PBEP Fractions	14
6	Fractionation of PBEP Extract	15
7	Properties of PECH Fractions	17
8	Evaluation of PECH Raffinate	18
9	Effect of Carbon Treatment on PBEP - 2nd Series	22
10	Reaction Conditions Employed in Continuous PBEP Unit and Thermal Stability of Products	26
11	Rate of Difluoramination of DEPECH at 60°C	27
12	Conditions for PBEP Production Run	29
13	Characterization of Solvent-Free Production Sample	30
14	Results of Curing Studies	30

CONFIDENTIAL

LIST OF FIGURES

<u>Figure</u>		Following Page
1	Diagram of PBEP Fractionation Equipment	9
2	Effect of PBEP Sample Size on Extraction Profile	10
3	Carbon Tetrachloride-Trichloroethane Elution Curve for PBEP .	10
4	PBEP Integral Molecular Weight Distribution Curve Based on Crude PBEP Fractions	10
5	Effect of Elimination of Contaminants on Integral Molecular Weight Distribution Curve of PBEP Sample No. 10001-186 . . .	11
6	PBEP 10001-186 - Differential Molecular Weight Distribution Curve	11
7	Variation of PBEP Properties With Fraction No.	11
8	Variation of Hydroxyl Content and Functionality in PBEP With Molecular Weight	11
9	Thermal Stability Variation in Fractionated PBEP	12
10	Relative Tensile Properties of PBEP Fractions	13
11	Carbon Tetrachloride Extraction of PECH, DEPECH and PBEP . .	14
12	Tensile Properties of PBEP Cures with a) Regular PBEP and b) PBEP Raffinate	15
13	Effect of Solvent Composition on PECH Extraction	16
14	Tensile Properties of PBEP From PECH Raffinate	19
15	Effect of Dibutyltin Diacetate Concentration on TDI-PBEP Reaction	23
16	Deactivation of DBTDA by PBEP	23
17	Effect of PBEP Raffinate on Deactivation of DBTDA	23
18	Effect of Carbon-Treated PBEP on Deactivation of DBTDA . . .	23
19	Schematic Flow Diagram of Continuous PBEP Unit	25

CONFIDENTIAL

ENERGETIC BINDER PRODUCTION (U)

(C) Summary

(C) The energetic binder PBEP, poly[1,2-bis(difluoramino)-2,3-epoxypropane], is prepared in a three-step process consisting of (1) polymerization of epichlorohydrin, (2) dehydrochlorination of the polyepichlorohydrin (PECH) to poly(2,3-epoxypropene), DEPECH, and (3) difluoramination of the unsaturated polymer in acetone solution with tetrafluorohydrazine. A primary objective of the present program has been to construct and operate a continuous process for the difluoramination step.

(U) Polyepichlorohydrin has been prepared in a 200-pound batch. Five large batches of unsaturated polymer (DEPECH) were prepared including two 21-pound batches.

(C) A two-stage continuous reactor system for the difluoramination step has been constructed. Several process variables have been investigated and near optimum conditions were found to be 40% excess N_2F_4 , one hour residence time, 60°C first stage, 110°C second stage reaction temperature, 11%w solution of DEPECH in acetone as feed, and 400 psig pressure. The necessity for anaerobic storage of DEPECH was demonstrated. An upper limit of water content of solvent was established.

(C) A forty-pound sample of continuous product was accumulated and distributed to propellant contractors for evaluation. Evaluation of the continuous product in nonenergetic formulations showed it to be comparable to batch product.

(C) PBEP has been fractionated on the basis of molecular weight into ten fractions by solvent gradient elution. The polymer was deposited on a packing of Chromosorb W and eluted therefrom by a mixture of carbon tetrachloride and 1,1,1-trichloroethane of gradually changing composition. Since the hydroxyl functionality of PBEP varies with molecular weight a partial fractionation on the basis of functionality was also achieved. Thus mono-functional-rich low molecular weight and trifunctional-rich high molecular weight fractions were isolated while the mid-fractions had an improved (i.e., narrower) distribution both with regard to molecular weight and difunctionality.

(C) Extensive evaluation of the fractions has been carried out including analyses such as molecular weight, elemental and hydroxyl content, thermal stability measurements and small scale curing tests. The molecular weight distribution was plotted both in integral and derived differential form. Fraction molecular weights ranged from 1000 to 12000 and hydroxyl functionality from 1 to 3 OH groups per chain. Thermal stabilities ranged from approximately 4 cc/g/100 hr for the mid-fractions to 8-10 cc/g/100 hr for the high and low fractions.

CONFIDENTIAL

(C) Cure evaluation of selected fractions typical of a) the mid-fractions with narrower distribution both of molecular weight and hydroxyl functionality, b) the low molecular weight monofunctional fractions and c) the high molecular weight trifunctional fractions gave the following results:

1. No significant change in the tensile properties of the mid-fractions.
2. Very poor properties for the low fractions in keeping with their low functionality.
3. A 30-40% increase in the tensile strength of the high fractions.

(C) Exhaustive extraction with carbon tetrachloride of PBEP deposited on Chromosorb W has resulted in the separation of PBEP into two fractions, a CCl_4 -soluble extract, comprising 20-25%w, with a molecular weight of 1500-1800 and hydroxyl functionality of 1.0-1.2, and a CCl_4 -insoluble raffinate, comprising 75-80%, with a molecular weight of 5000-6000 and hydroxyl functionality of 2.4-2.6. The extract is the less thermally stable fraction by approximately 50%. Cure evaluation of the more promising raffinate fraction has been carried out with the following conclusions:

1. Raffinate PBEP, unlike regular PBEP, can be cured successfully without the addition of crosslinker. Cure properties are somewhat poorer than with regular PBEP containing 2 phr glycerol but, with optimization, would very probably be satisfactory where a minimum of added nonenergetic ingredients is desired.

2. Increased tensile strengths were obtained, ranging with crosslinker level, from 85% increase at 1 phr to 18% at 3 phr. In comparison with regular PBEP similar tensile values were obtained with the raffinate polymer at approximately half the crosslinker level. Elongations were correspondingly lower but still satisfactory.

(C) The possibility of fractionating the polymer at an earlier and less expensive stage in the synthesis has been investigated. Polyepichlorohydrin (PECH) has been separated into two fractions by extraction with a solvent mixture of 60% CCl_4 - 40% cyclohexane. The raffinate sample had a molecular weight of 3700 and an OH functionality of 2.7. Evaluation of the latter by conversion to DEPECH and PBEP showed that the polymer's superior properties were retained through the DEPECH step but that degradation during the difluoramination step resulted in the loss of OH functionality and the generation of low molecular weight monofunctional polymer. Consequently the improvement in PBEP cure properties was somewhat less than with the PBEP raffinate and the polymer could not be cured without added crosslinker.

(U) A number of attempts were made to fractionate the polymer at the DEPECH stage. While several polymer fractions were obtained a completely successful procedure could not be achieved due to their instability.

CONFIDENTIAL

(C) The carbon treatment of PBEP has been investigated. Substantial improvements in thermal stability (1.5-2.5 cc/g/100 hr compared with normal values ranging from 4-8 cc/g/100 hr) were observed with some loss of fluorine content. An additional and significant advantage of carbon treatment appears to be a reduction in the cure catalyst deactivation caused by PBEP.

(C) Small scale cure studies involving reaction of tolylene diisocyanate (TDI) with PBEP, glycerol and water have been carried out. An infrared technique was used to monitor the TDI consumption. Catalyzed (dibutyl tin diacetate, DBTDA) and uncatalyzed systems were surveyed. The technique was used to detect catalyst deactivation by a component, probably HF, in the PBEP and to compare the effect of various PBEP treatments on the deactivation process. It was shown that the deactivation could be essentially eliminated by treating the PBEP with carbon.

(C) The stability of PBEP in the methylene or ethylene chloride solution used for shipping or storage of the polymer was investigated. The PBEP in dry samples and with varying amounts of water present was shown to be essentially unchanged after 8 months at -10°C or after 4 weeks at 50°C.

CONFIDENTIAL

ENERGETIC BINDER PRODUCTION (U)

(C) The Fractionation of PBEP

(C) Introduction

(C) The energetic binder PBEP, poly[1,2-bis(difluoramino)-2,3-epoxypropane], is prepared by Shell Development Company for evaluation by a number of Air Force propellant contractors. Typical properties of the polymer as presently produced in our continuous reactor are given in Table 1.

Table 1. PROPERTIES OF PBEP (10001-186)

C, %w	24.5
H, %w	3.5
N, %w	15.8
NF ₂ , %w (based on N)	58.7
F, %w	40.5
F/N Ratio	1.89
Molecular Weight (vapor pressure osmometer)	3900
Hydroxyl, ^a eq/100 g	0.045
functionality	1.8
Thermal Stability at 80°C, cc/g/100 hr	5.2
after 200 hr	

a) Determined by infrared technique based on poly(propylene glycol) calibration.

(C) In common with the vast majority of polymers, PBEP contains polymer chains covering a range of molecular weights with the repeating units varying from a few up to perhaps 100 or more with an average of about 25. The hydroxyl functionality is also an average value since hydroxyl terminations per polymer chain can vary from one (or perhaps even zero) to three. Both the distribution of molecular weight and of hydroxyl functionality, but especially the latter, can play a substantial part in determining the physical properties of cured propellants containing PBEP as the binder ingredient.

(C) The separation of PBEP into a number of different fractions and subsequent examination of these fractions are desirable for a variety of reasons. These include information that may be obtained on the course of the PBEP synthesis, especially if comparisons can be made with fractionations carried out on PBEP intermediates such as polyepichlorohydrin (PECH) or poly(2,3-epoxypropene) (DEPECH). On a practical level there are questions related to the possibility that substantial improvement in properties such as thermal stability and propellant cure characteristics may result from the use of certain PBEP fractions, selected, possibly on the basis of molecular weight, but more likely on the basis of their hydroxyl functionality. For example, removal of monofunctionally terminated species with their propensity for effecting chain terminations suggests that fractionation by hydroxyl functionality would be a desirable goal. However it was concluded that such

CONFIDENTIAL

a fractionation would be difficult to achieve directly especially with a polymer such as PBEP where the polar effect of the relatively few hydroxyl groups is likely to be overshadowed by the many difluoramino and ether groups. Consequently our efforts have concentrated in the main on achieving a fractionation based on molecular weight since, as will become apparent, hydroxyl functionality in PBEP is to a certain extent dependent on molecular weight.

(U) Polymer fractionation techniques capable of handling appreciable quantities of polymer can be classified under two major headings, precipitation methods and chromatographic or fractional solution methods. In a typical precipitation procedure successive quantities of a nonsolvent are added to a solution of the polymer and the precipitated fractions isolated by decantation after a suitable settling period, generally at least 24 hours. Advantages are that relatively large quantities of material can be fractionated for further evaluation. However for maximum separation efficiency very dilute solutions must be used (1% or, even better, 0.1%) with the result that extremely large solvent (and nonsolvent) volumes are involved if substantial quantities of the polymer fractions are required. Furthermore an inherent weakness in fractional precipitation methods is the "tail effect" which results in every fraction containing an appreciable amount of the lower molecular weight components. This defect is absent from fractional solution methods.

(U) Fractional solution techniques take advantage of the variation in polymer solubility with molecular weight by extracting the polymer with a solvent system of progressively increasing power. This goal may be achieved in a number of different ways, the most common of which are by the establishment of a thermal gradient in the column containing the polymer and by the continuous addition of a solvent to a fixed volume of nonsolvent in a solvent gradient elution technique. Advantages of the method include elimination of the "tail effect" and the use of relatively small solvent volumes, the latter allowing the convenient fractionation of practical quantities of polymer. Thus it is obvious that fractional solution methods are most suited to our purpose which is the separation of substantial amounts of PBEP into clean-cut, well-defined fractions.

(C) Fractionation by Precipitation

(U) At an earlier stage in the development of the PBEP synthesis a simple fractionation of the crude PBEP was carried out by the addition of petroleum ether to a methylene chloride solution of the PBEP. The bulk of the polymer was precipitated leaving a few percent of lower molecular weight, less thermally stable polymer still in solution. This procedure and a few related experiments using varying amounts of the precipitating solvent had demonstrated the variation in molecular weight with increased addition of the petroleum ether and had shown in addition that the hydroxyl functionality of the polymer varied with the molecular weight.

(C) While little further use of this fractionation technique has been made at Shell Development due to the objections cited above the method has been used to make rapidly available a relatively small quantity of a few PBEP

CONFIDENTIAL

fractions for examination by workers at Dow and Lockheed as part of their program of kinetic studies on the decomposition of NF_2 -containing compounds. The fractions representing successively 30% and 22% of the polymer were precipitated by the addition of successive quantities of petroleum ether to 50 g PBEP in 4.3%w solution in methylene chloride. The precipitate was allowed to settle overnight before separation by decantation. A comparison of the physical properties of the two fractions and the original whole polymer are given in Table 2.

(C) Table 2. PROPERTIES OF PRECIPITATED PBEP FRACTIONS

Properties	Whole Polymer	High Fraction	Intermediate Fraction
Polymer Fraction, %w	100	29.6	21.9
C, %w	25.9	26.1	26.1
H, %w	3.2	3.2	3.3
N, %w	15.7	15.9	16.0
NF_2 , %w (based on N)	58.4	59.1	59.4
F, %w	41.4	41.1	41.4
Molecular Weight (vapor pressure osmometer)	3800	6700	5200
Hydroxyl, ^{a)} eq/100 g functionality	0.042 1.6	0.038 2.6	0.046 2.4
Thermal Stability at 80°C, cc/g/100 hr after 200 hr	4.8	5.4	5.7

a) Infrared method based on poly(propylene glycol) calibration.

(U) The data confirm that some degree of separation by hydroxyl functionality has taken place in the course of the molecular weight separation. The differences in the thermal stabilities are barely significant.

(C) Fractionation by Solution

(U) Fractionation on Silica Gel

(U) Workers at Esso as part of their program to develop accurate techniques for the analysis of PBEP have carried out a considerable amount of work on the fractionation of PBEP on silica gel.^{a)} While the polar nature of this packing might be expected to aid in the fractionation of PBEP based on

a) Esso Quarterly Report No. 2, January-March 1967, GR-2-FBP-67; Esso Quarterly Report No. 4, July-September 1967, GR-4-FBP-67; Contract No. FO4611-67-C-0012.

UNCLASSIFIED

the OH content as desired by Esso the results were found to be somewhat less than clear-cut and with the additional bad feature that some degradation to nitrile seemed to have taken place. Because of the desirable features associated with a fractionation achieved on the basis of hydroxyl functionality, at least from the point of view of improved polymer cure performance, it was decided to take a further look at the possibilities of PBEP fractionation on this packing.

(U) PBEP samples dissolved in benzene or chloroform were passed through silica gel columns using a packing/PBEP ratio of approximately 70/1, i.e., similar to Esso. While elution with either of these solvents gave recoveries of approximately 50%, again similar to Esso, it was disturbing to note that the bulk of this material seemed to elute virtually at the solvent front. That is, the possibility existed that at least some of this 50% polymer was being eluted, not because it was different from the remaining noneluted 50%, but simply because the column was overloaded at the 70/1 ratio. This was confirmed when the experiment was repeated with a portion of the eluted PBEP again using a packing/PBEP ratio of 70/1. The same proportion of recovered PBEP was obtained. Further confirmation came with an increase in the packing/PBEP ratio to 144/1 when only approximately 18% of the PBEP was immediately recoverable in the benzene eluent. PBEP retention was even more complete using chloroform and with a ratio of 160/1; no PBEP was eluted with the chloroform.

(U) While these results suggested that it was possible to operate a silica gel column properly, that is, so that the PBEP was freely retained on or released from the column as the PBEP-silica gel interaction dictated, it was obvious that the much higher than anticipated packing/polymer ratio would substantially limit the quantities of PBEP that could be handled. For the purpose of analysis, however, a small scale run was made in which ~3 g PBEP was adsorbed from chloroform solution on 495 g SiO₂ and eluted by the progressive addition of acetone to the CHCl₃ eluant. Only 65% of the PBEP could be recovered. Even the substitution of 100% acetonitrile as eluant yielded no more PBEP. Thus one of the prime requirements of a satisfactory fractionating system, that a quantitative polymer recovery be made, could not be met by the silica gel system. An additional undesirable feature was the considerable increase in the size of the small nitrile infrared band at 4.45 μ sometimes observed in PBEP samples. This evidence for silica gel induced polymer degradation has already been noted by the Esso workers. As a consequence of these results, it was decided not to pursue further the use of silica gel in fractionating PBEP.

(U) Fractionation on Chromosorb W

(U) With the failure of the silica gel system described above with its emphasis on fractionation based on polarity differences and hence on variations in the hydroxyl content of the various polymer chains it was decided to concentrate on achieving a fractionation based on molecular weight differences. This had the immediate advantage that we were now looking for an inert packing that had no adsorptive capacity for the polymer and therefore would a) be less likely to cause polymer degradation and b) allow for more

UNCLASSIFIED

ready and more complete recovery of the polymer. A likely source for such a packing appeared to be carriers used in gas chromatography since similar requirements of low polarity and adsorptive capacity are desirable to minimize peak tailing effects. Preliminary tests were therefore made with Chromosorb W, using the acid-washed variety to reduce further the possibility of degradation. It was quickly established that a) PBEP could be readily recovered from a Chromosorb W column with 95-100% efficiency by elution with methylene chloride and b) there was no appreciable degradation after 1-2 days' contact with the column.

(U) Solvent Selection. In the solvent gradient method which it was planned to use for the fractionation a critical factor in obtaining optimum separation is the selection of the best solvent-nonsolvent combination. It is desirable to spread the polymer fractions over as wide a range of solvent-nonsolvent compositions as possible and to achieve this it is necessary to use a "poor" solvent and a "good" nonsolvent, that is, a solvent which barely dissolves the polymer and a nonsolvent which almost dissolves it. A number of potential solvents (and nonsolvents) were selected on the basis of a comparison of their solubility parameters and those of known solvents for PBEP and a series of tests was made comparing the rate of solution of 0.5 g portions of PBEP. The results are summarized in Table 3.

Table 3. RATE OF SOLUTION OF PBEP IN VARIOUS SOLVENTS

Solvent	Solubility Parameter	Time to Dissolve PBEP, min
Propyl chloride	8.5	5
Methylene dichloride	9.7	6
Ethylene dichloride	9.8	6
Butyl chloride	8.4	9
1,1,1-Trichloroethane	8.7	10
Benzene	9.2	17
Toluene	8.9	17
Hexyl chloride	8.3	18
Mesitylene	8.8	insoluble
Carbon tetrachloride	8.6	insoluble
Cyclohexane	8.2	insoluble

(U) While the PBEP appeared to be insoluble in the three nonsolvents close inspection revealed differences in a) the degree of smearing or spreading of the polymer on the walls of the vial and b) the slight haziness that developed. These observations suggested that there was some slight interaction

UNCLASSIFIED

between PBEP and carbon tetrachloride or mesitylene. Of these two, carbon tetrachloride was selected as the nonsolvent on the basis of its lower boiling point and hence ease of removal. Trichloroethane (TCE) was selected as the solvent on the basis of its relatively poor solubility characteristics, its high volatility (ease of removal), its ready availability and low cost and the fact that it belonged to the same solvent family as CCl_4 .

(U) Equipment. The apparatus used in the fractionation work is shown in Figure 1. It consists essentially of two sections: 1) the fractionating column and associated fraction collecting equipment and 2) the solvent pumping and mixing system. The column is a glass tube 1-meter long with an ID of 50 mm. Since the column is operated in a reverse flow mode to minimize channeling effects and increase pumping accuracy the packing is topped with a thin layer of glass wool and a sintered glass disk to prevent upsurges. The eluent take off tube is adjusted to the correct length to serve as a hold down on the glass disk. The second tube in the column headspace is used to regulate the pressure in the headspace so that the liquid head in the column is held at a minimum, i.e., slightly above the surface of the glass disk. The solvent pumping and mixing system consists of a lapp pump, two feed reservoirs, one for solvent and the other for nonsolvent, and a mixing vessel. When the solvent gradient technique is being used the mixing vessel is filled initially with the nonsolvent and stirred magnetically. Pumping from the nonsolvent reservoir into the mixer and up through the column packing is then started. If the polymer is really insoluble in the nonsolvent the procedure up to this point will serve merely to check out the operation of the system. However in the case of PBEP where the polymer was found to be partly soluble in the nonsolvent, carbon tetrachloride, it was necessary, to ensure run to run reproducibility, to pump a definite quantity of "nonsolvent" relative to the amount of PBEP being fractionated. The feed is then switched to the solvent, the concentration of which then builds up progressively in the mixer in logarithmic fashion. The composition of the solvent-nonsolvent mixture at any time thereafter may be calculated from the following equation,

$$\phi = C_B - (C_B - \phi_0)e^{-rt/V_0}$$

where ϕ_0 = volume fraction of solvent in mixing chamber at start
 ϕ = volume fraction of solvent in mixing chamber at time t
 C_B = volume fraction of solvent in liquid pumped to mixer
 r = volume of solvent-nonsolvent withdrawn in unit time
(i.e., pumping rate)
 V_0 = volume of mixing chamber.

(U) The PBEP polymer was deposited on the column from methylene chloride solution. In a typical case 30 g PBEP dissolved in ~830 g MDC was poured down a column containing ~350 g acid-washed Chromosorb W. This volume of solution was sufficient to wet the packing to within approximately 1 in. of the bottom. The methylene chloride was then removed with a stream of nitrogen.

(U) Fractionation efficiency is affected by the ratio of extracting solvent volume to weight of polymer. The latter may be varied either by

UNCLASSIFIED

UNCLASSIFIED

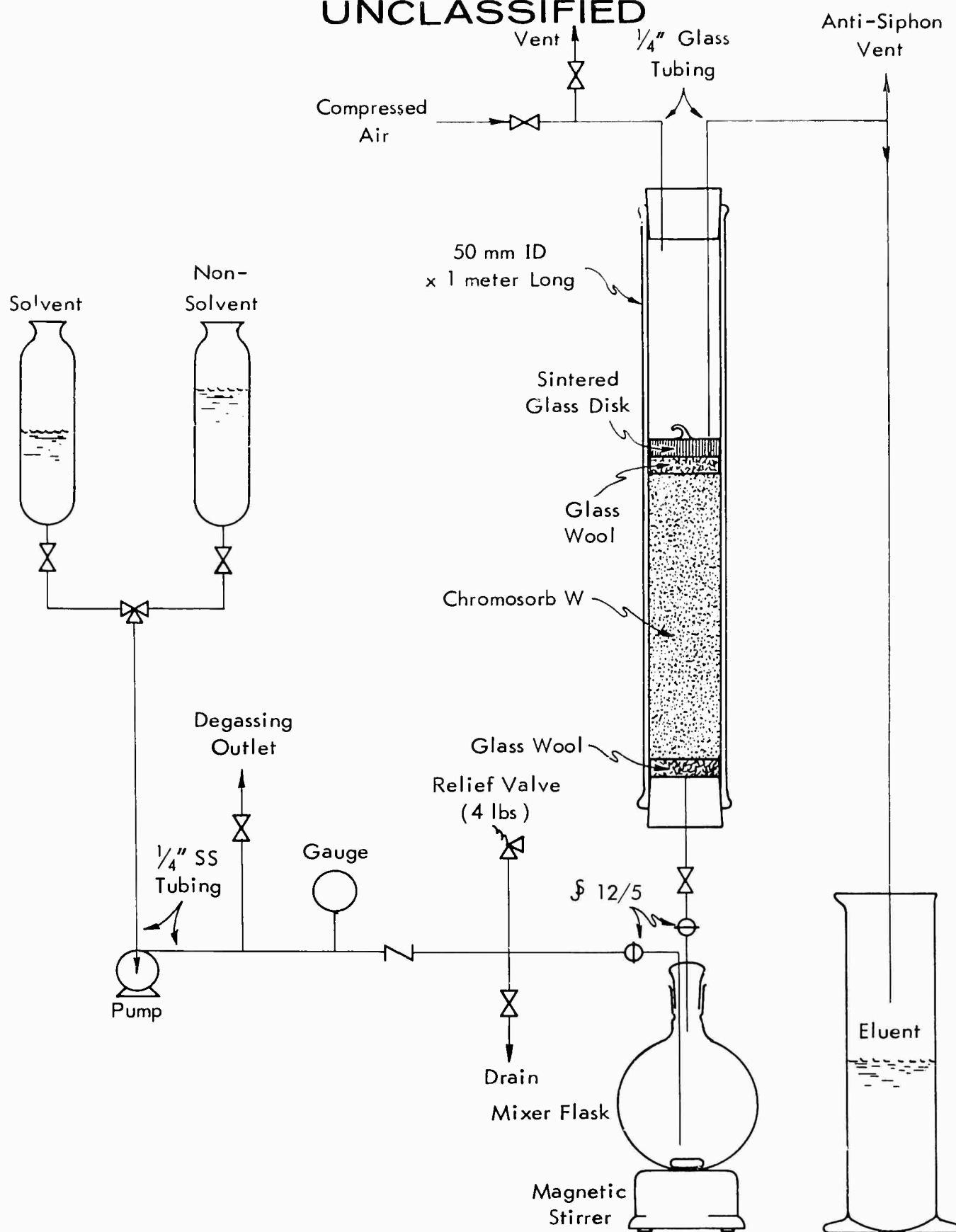


Figure 1. DIAGRAM OF PBEP FRACTIONATION EQUIPMENT

AFRPL-TR-68-184
64599

UNCLASSIFIED

UNCLASSIFIED

changing the size of the mixer vessel or by varying the amount of PBEP being fractionated. For maximum effectiveness in separation it is obvious that there must be present a sufficient quantity of any instantaneous solvent-nonsolvent mixture to extract all the polymer that is capable of being dissolved by that solvent composition. The effect of varying the polymer/total solvent ratio is seen in Figure 2. The ratio was varied by varying the PBEP from 10-30 g. The total quantity of solvent mix and the size of each eluent fraction were kept constant (with the exception of fraction 1 which was extracted with a volume of pure CCl_4 proportional to the size of the PBEP sample; the then expected and necessary constant proportion of PBEP extracted in this fraction was confirmed). It will be seen that there is a considerable proportion of potentially extractable low molecular weight polymer in the 30 g and, to a lesser extent, the 20 g samples which was not extracted. While ideally it would have been desirable to have continued reducing the size of the sample until essentially no further change in the distribution of the polymer took place it was felt that operating at the 10 g scale in the apparatus described above represented a satisfactory compromise between efficiency and the need for sizeable quantities of fractionated polymer.

(U) The equipment was operated in the solvent gradient procedure outlined above when it was desired to separate the PBEP into ten fractions. In order to obtain equal sized fractions for convenience in using them for test purposes the volumes of the various eluent fractions were adjusted appropriately using the elution curve shown in Figure 3.

(U) The equipment was also used in the carbon tetrachloride extraction work also described in this report with the substitution of a short piece of tubing for the mixer vessel. Two sets of apparatus were eventually constructed to handle the demand for PBEP fractions and CCl_4 -extracted PBEP.

(U) Fractionation by Solvent Gradient Elution

(U) Using the equipment and procedures described above a series of fractionations have been carried out on samples of PBEP ranging from 2 g through 10 g and 20 g up to 30 g. As mentioned earlier the latter size appeared to be too great for our system. Consequently in our later work where a repetitive series of fractionations was carried out with the main goal of obtaining a sufficient amount of each fraction for evaluation in a cure system the quantity of polymer per fractionation was reduced to 10 g.

(U) The PBEP was fractionated into from eight to ten fractions which were found to range in molecular weight (determined by Vapor Pressure Osmometer) from 1300 to approximately 7000-8000 measured on the crude fractions. However the highest molecular weight crude sample was not fraction 10. This is a result of the inversion shown in Figure 4. Fraction reversal behavior has been recorded many times in the literature where it has been attributed to the manner in which the polymer is deposited on the packing. However in the present instance the major part of the problem appeared to derive from two other sources, a) contamination from Kel F stopcock grease and b) traces of higher boiling impurities in the solvent system. Stopcock contamination proved to be a problem with all types of commercial greases and was only eliminated by the use

UNCLASSIFIED

UNCLASSIFIED

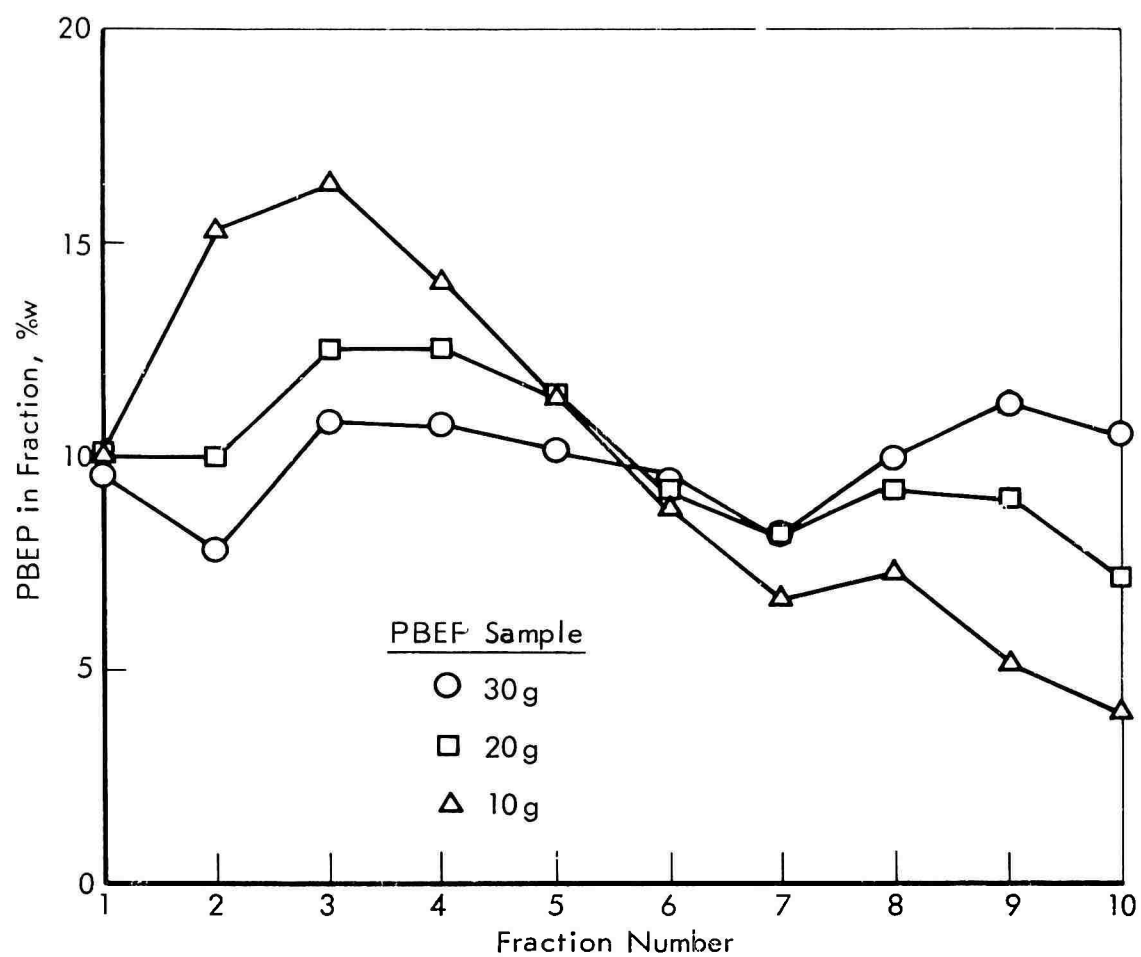


Figure 2. EFFECT OF PBEP SAMPLE SIZE ON EXTRACTION PROFILE

AFRPL-TR-68-184
64599

UNCLASSIFIED

UNCLASSIFIED

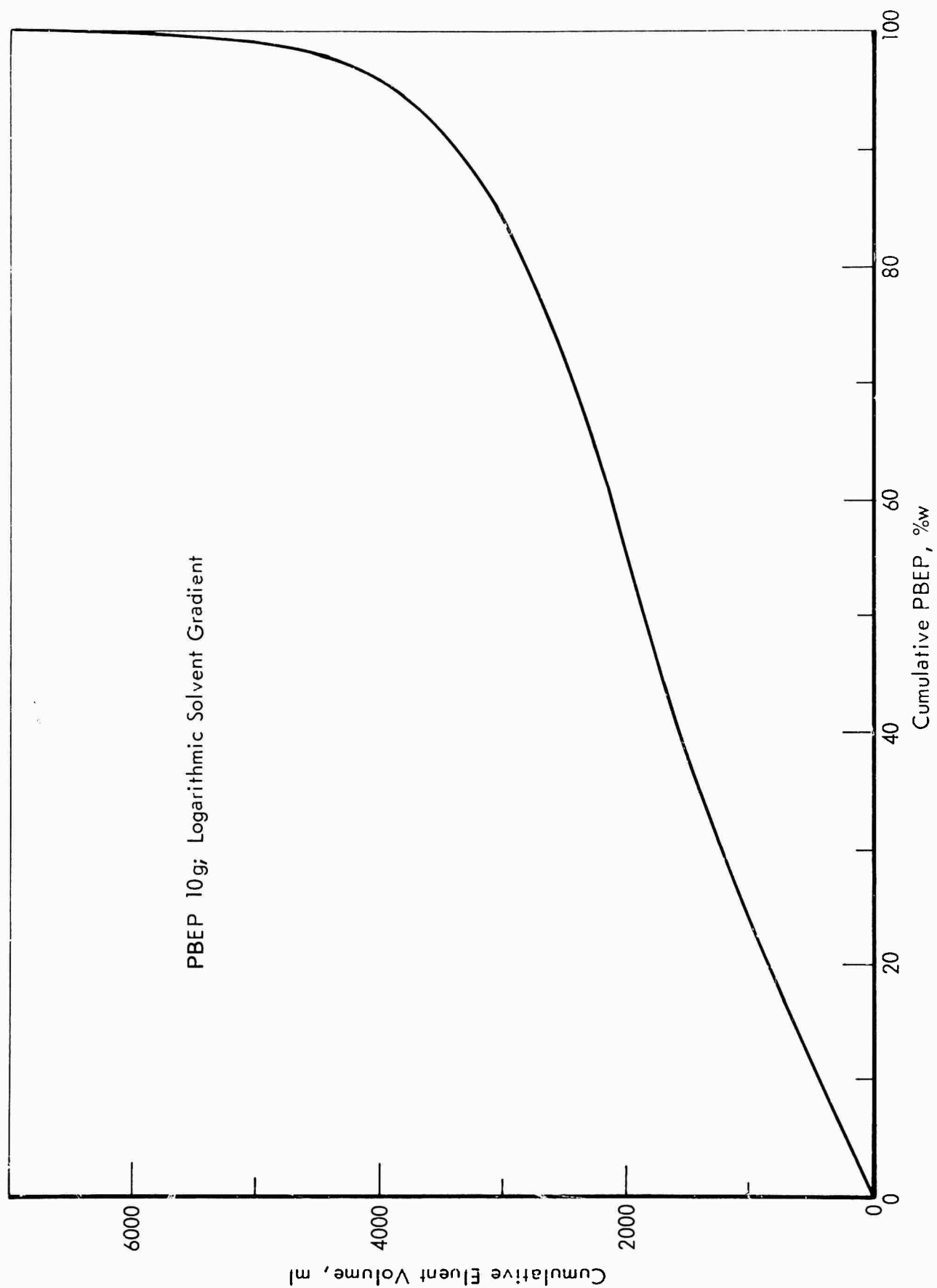


Figure 3. CARBON TETRACHLORIDE - TRICHLOROETHANE ELUTION CURVE FOR PBEP

AFRPL-TR-68-184
64599

UNCLASSIFIED

UNCLASSIFIED

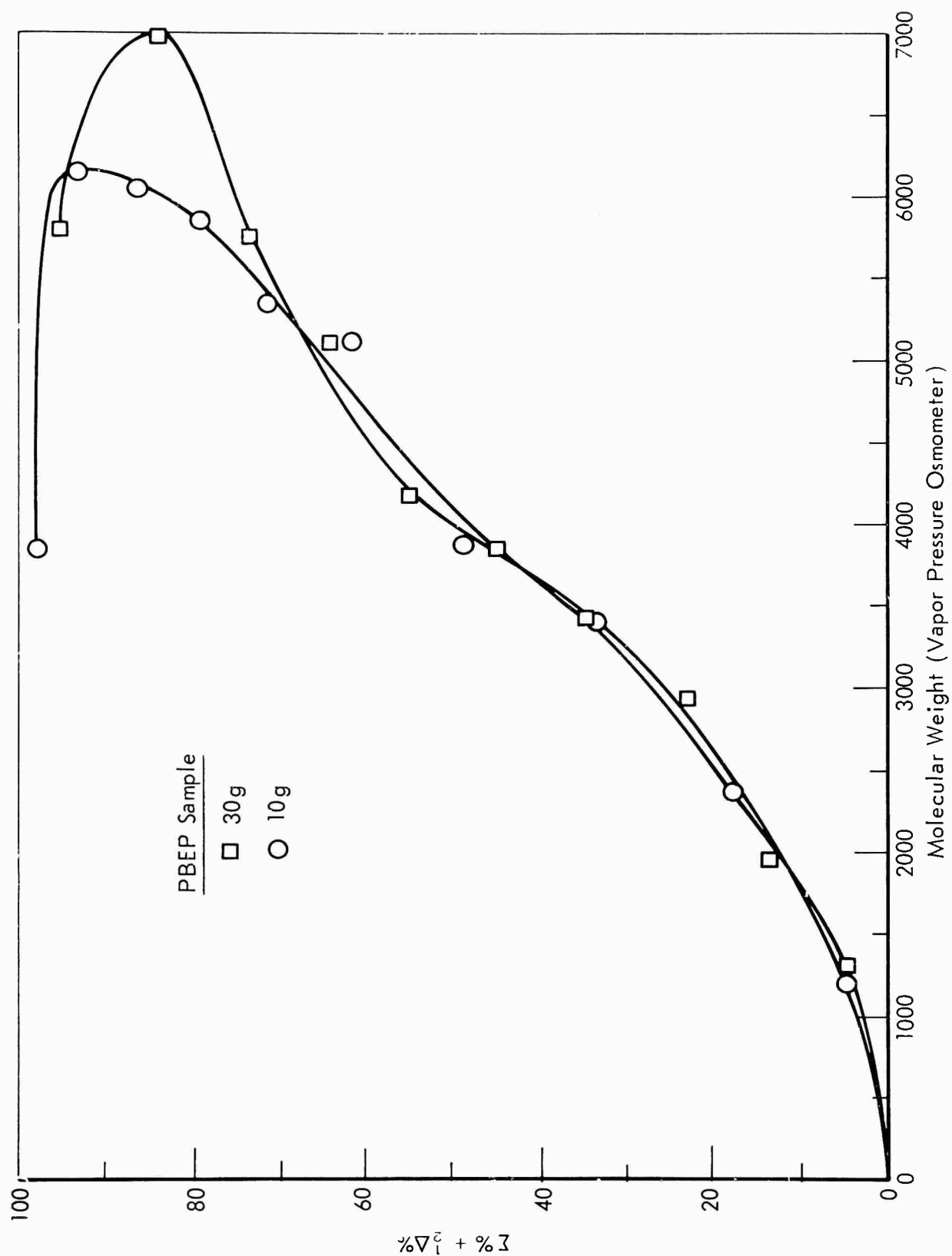


Figure 4. PBEP INTEGRAL MOLECULAR WEIGHT DISTRIBUTION CURVE BASED ON CRUDE PBEP FRACTIONS

AFRPL-TR-68-184
 64599

UNCLASSIFIED

UNCLASSIFIED

of teflon stopcocks or, where this was not feasible, by lubrication with a home-made grease consisting of glycerol and talcum powder. The improvement effected by this modification is shown in Figure 5 where the left-hand curve is the curve obtained from the crude fractions from a 20 g fractionation. The fact that the typical S-shaped distribution curve was still not obtained is explained by the solvent contaminants already mentioned. While their effect in the lower and middle molecular weight ranges is relatively minor this is not the case in the high molecular weight fractions. Furthermore the effect was intensified by the fact that in order to collect roughly equal sized weight fractions much larger eluent volumes (up to 10 times greater for Fraction 10) had to be collected in order to isolate the last fractions. Since the level of these solvent derived impurities would not be greater than 1 or 2% even in the worst case (i.e., fraction 10) and therefore would not be expected to have any significant effect on the properties of the fractions of most practical interest, namely cure properties and thermal stability, it was not considered necessary to embark on the meticulous and time consuming program which would have been required to produce the large volumes of ultra-pure fractionating solvents necessary to overcome this problem. However in order to obtain at least an approximate idea of the true molecular weight distribution curve a few selected fractions were "purified" by precipitation from methylene chloride solution. The fractions chosen were 1, 2, 9 and 10, all isolated with larger volumes of solvent, and, for comparison, a mid-fraction, number 6. The second curve in Figure 5 shows the typical S-shape obtained using the data from these purified fractions. It will be seen that the molecular weight of the PEEP fractions has been extended and now ranges from 1500 to greater than 11,000. The differential distribution curve derived graphically from these data is shown in Figure 6. The distribution appears to have a relatively flat top with a sharp drop off at both the high and low ends.

(U) Evaluation of Polymer Fractions

During the initial fractionation runs when the isolated fractions were too small for regular property analyses or cure studies an infrared survey of the fraction-to-fraction variation of absorption due to hydroxyl, carbonyl and nitrile groups was made. While the former is an essential component of the PEEP molecule the latter two groups are undesirable "impurities" generally present in small amount if at all. In Figure 7 the infrared absorbances for these groups are plotted together with the thermal stabilities of the fractions. Increases, relatively small, in both carbonyl and nitrile with increasing fraction number (i.e., increasing molecular weight) were observed while the hydroxyl content decreased in the expected manner. No pronounced correlation of thermal stability values could be detected with variations in any of these groups.

(U) More accurate determinations of hydroxyl content and functionality were made later by a quantitative infrared technique, calibrated with poly-(propylene glycol). The variation of these parameters with molecular weight is shown in Figure 8. It will be seen that:

1. Hydroxyl functionality levels off at 3, theoretically the highest possible value.

UNCLASSIFIED

UNCLASSIFIED

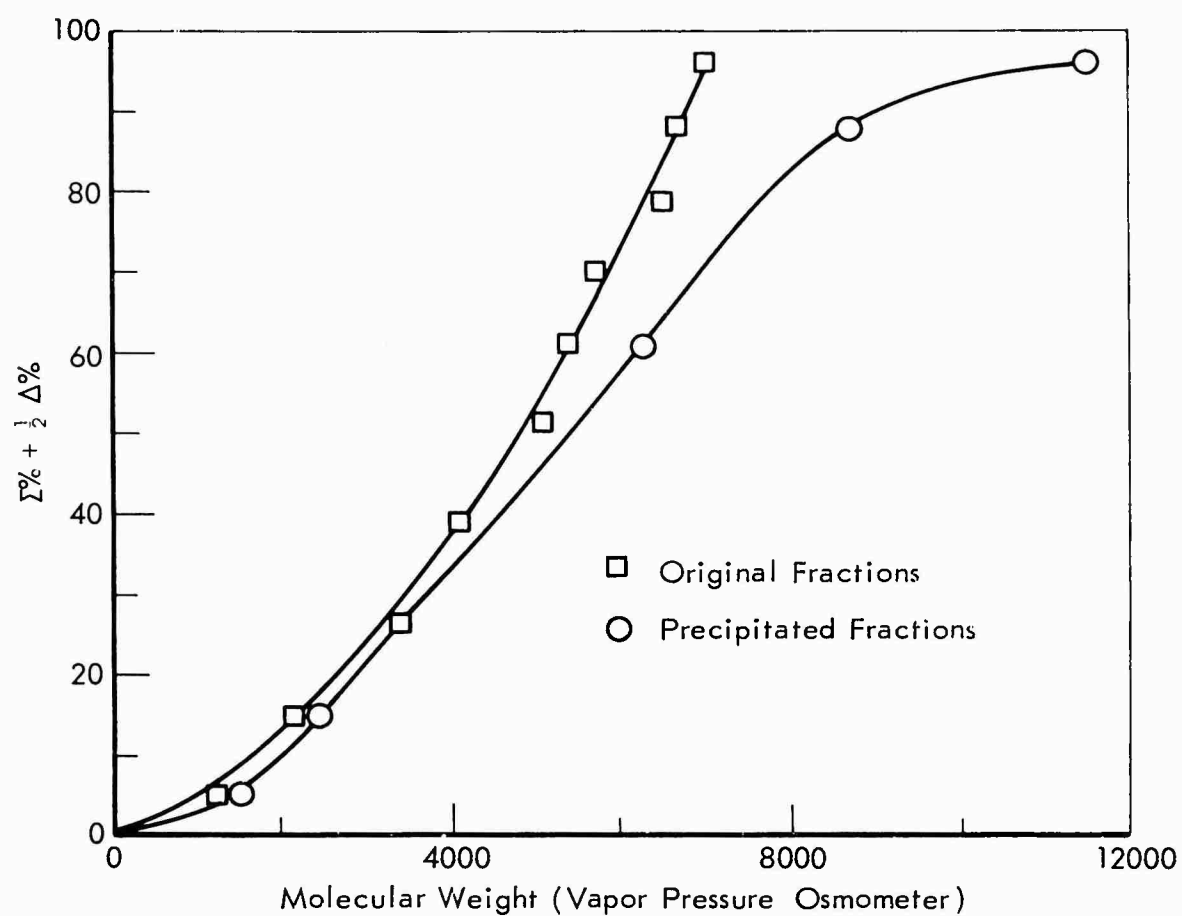


Figure 5. EFFECT OF ELIMINATION OF CONTAMINANTS ON
INTEGRAL MOLECULAR WEIGHT DISTRIBUTION CURVE OF
PBEP SAMPLE NO. 10001-186

AFRPL-TR-68-184
64599

UNCLASSIFIED

UNCLASSIFIED

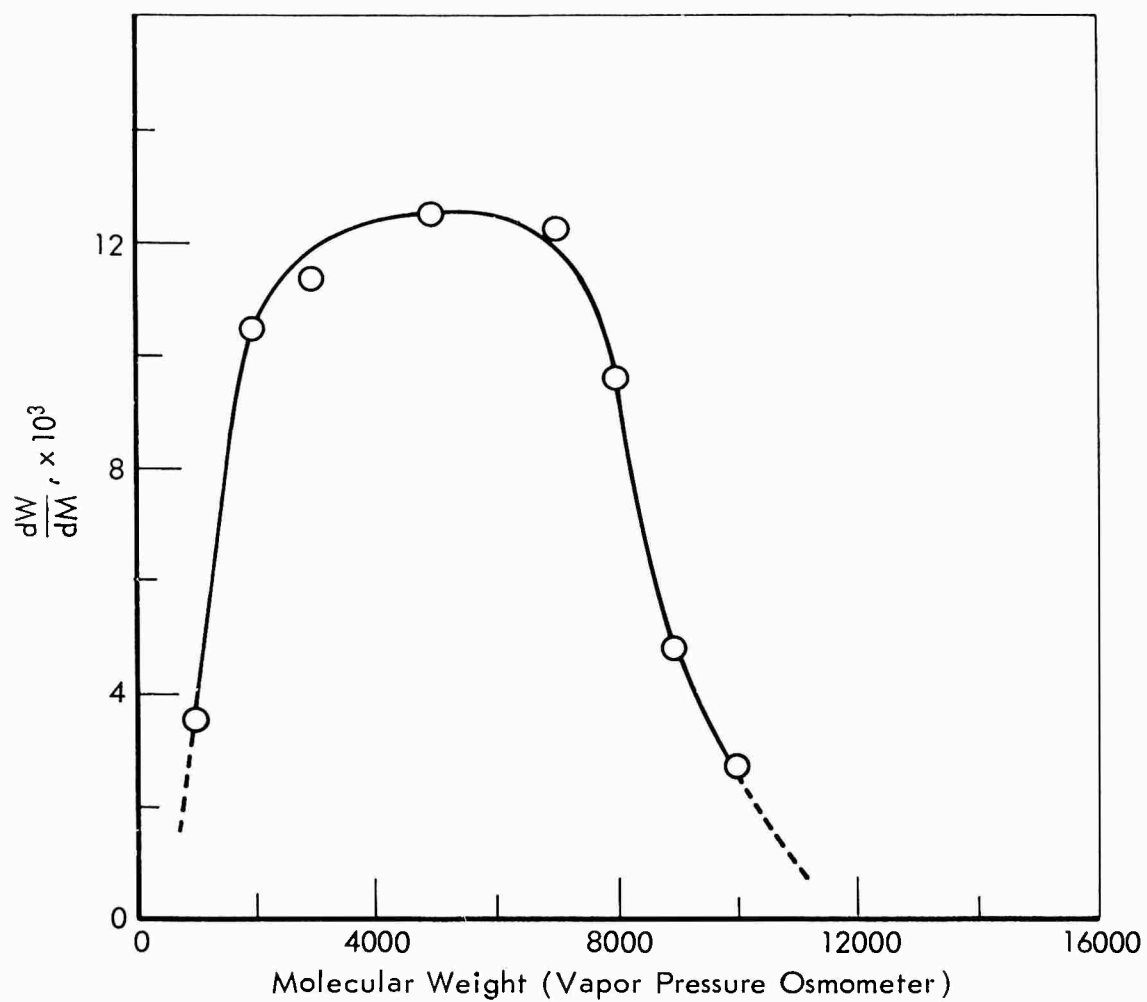


Figure 6. PBEP 10001-186: DIFFERENTIAL MOLECULAR WEIGHT
DISTRIBUTION CURVE

AFRPL-TR-68-184
64599

UNCLASSIFIED

UNCLASSIFIED

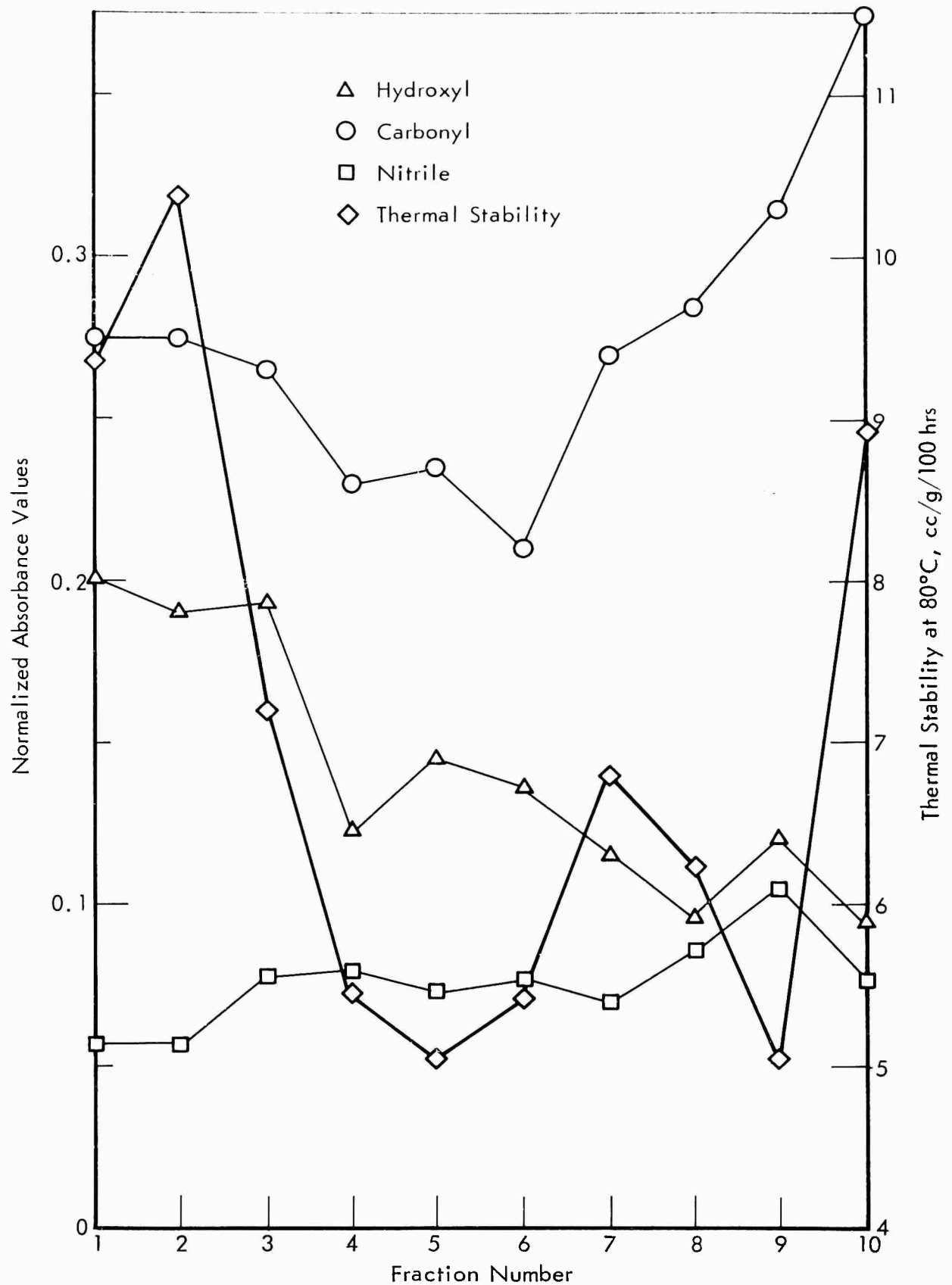


Figure 7. VARIATION OF PBEP PROPERTIES WITH FRACTION NUMBER

AFRPL-TR-68-184
64599

UNCLASSIFIED

UNCLASSIFIED

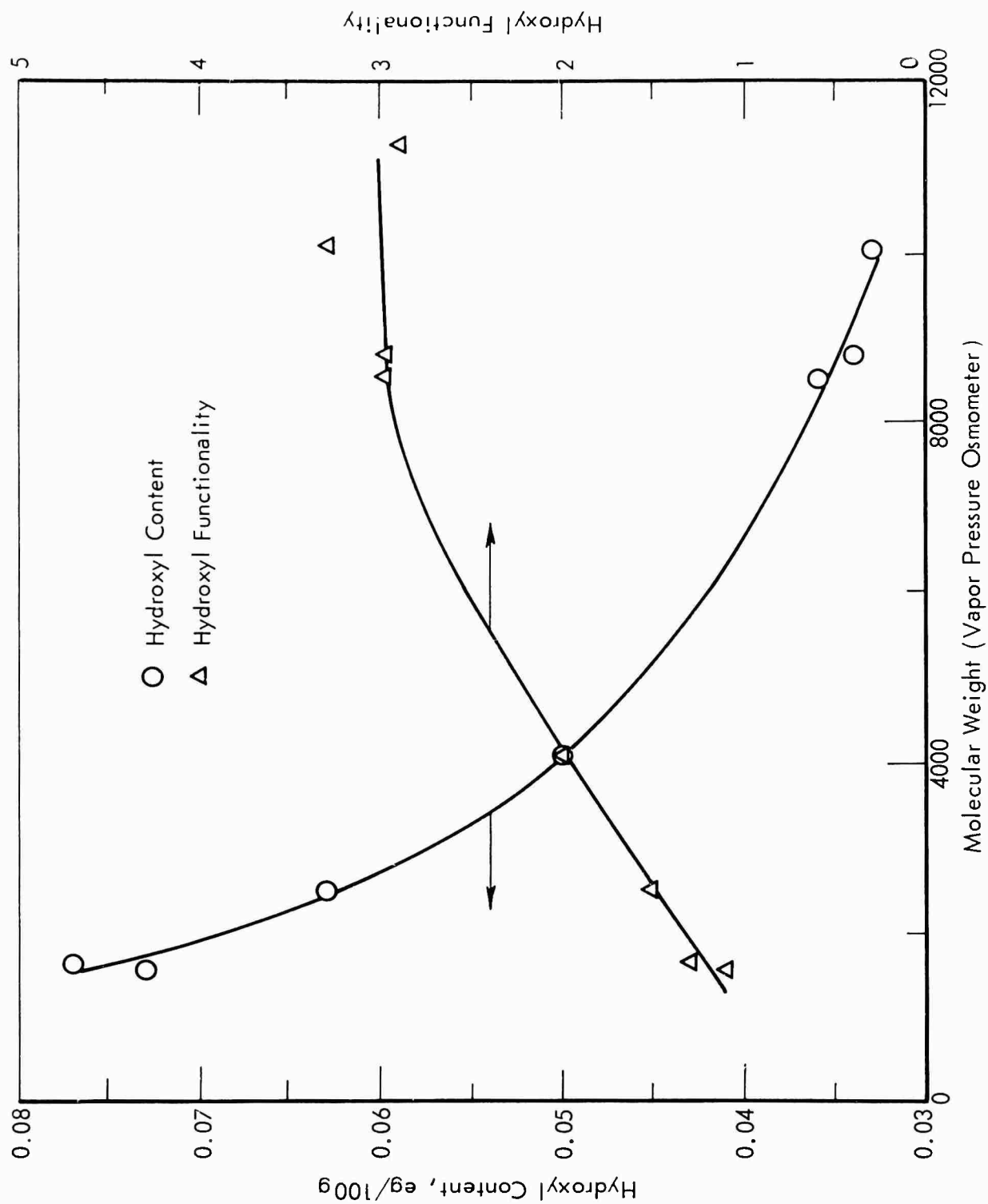


Figure 8. VARIATION OF HYDROXYL CONTENT AND FUNCTIONALITY IN PBEP WITH MOLECULAR WEIGHT

AFRPL-TR-68-184
64599

UNCLASSIFIED

UNCLASSIFIED

2. All the polymer with molecular weight above approximately 6000 is trifunctional.

3. At the lower molecular weight end the functionality of the polymer is somewhat greater than 1.0 and moreover extrapolation down to monomer molecular weight range (~100) gives a value which is not much below 1, suggesting that there is very little nonfunctionally terminated low molecular weight polymer present.

4. Between 1500 and 8000 the average functionality changes linearly with molecular weight.

(U) A major reason for fractionating PBEP was to investigate the thermal stability of the various fractions. The possibility existed that PBEP contained minor quantities of some highly unstable species which would accumulate in certain fractions and whose removal would result in substantial improvements in the thermal stability of the polymer. As already shown in Figure 7 and confirmed with further data, displayed in somewhat different fashion in Figure 9, differences in thermal stability were found with the general trend being toward poorer thermal stability in the lowest and, somewhat unexpectedly, the highest molecular weight fractions. However the full range of thermal stability values is relatively small, two to threefold at most and therefore removal of any one or two fractions from the main polymer has a relatively minor effect on the overall thermal stability. It can be concluded from this that the species responsible for the thermal instability in PBEP are not isolated units but instead are integral parts of the polymer structure at all molecular weight levels. Hence any improvement, if possible, may have to come from destruction or conversion of these units rather than their physical removal. A later section of this report will discuss recent work trending toward this goal.

(U) Another primary goal of the polymer fractionation work has been an evaluation of the cure properties of the various polymer fractions. As was already known and as the above data amply confirm, PBEP contains polymer chains with hydroxyl functional terminations ranging from three groups per chain down to zero. Since functionality has been shown to vary with molecular weight it was anticipated that improvements in curing might be expected for the following reasons:

1. Elimination of a substantial proportion of the monofunctionally terminated polymer by discarding the lower molecular weight fractions. Such material is probably the least desirable component in regular PBEP since it may interfere with the curing process by causing chain termination and consuming tolylene diisocyanate.

2. Preparation of medium molecular weight fractions which more closely approach pure difunctionality (as opposed to average difunctionality) than anything hitherto achieved. This claim is based on the elimination of substantial proportions of low molecular weight monofunctional and high molecular weight trifunctional material. There was a strong possibility that this "purer" polymer when used with added crosslinker would give improved cures, i.e., higher tensile strength.

UNCLASSIFIED

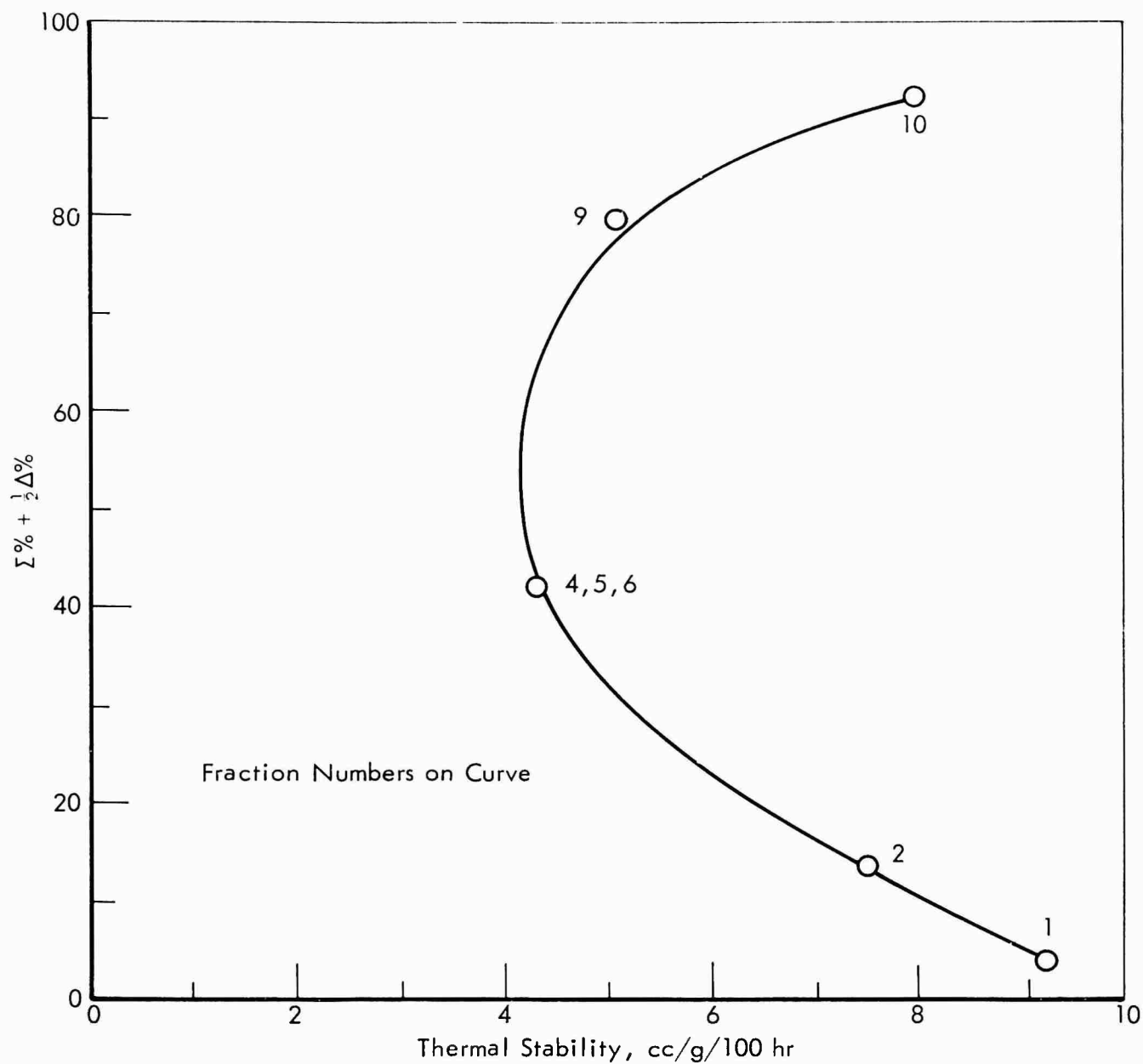


Figure 9. THERMAL STABILITY VARIATION IN FRACTIONATED PBEP

AFRPL-TR-68-184
64599

UNCLASSIFIED

CONFIDENTIAL

(U) Cure evaluation of the polymer fractions was severely limited by the quantity of polymer that could reasonably be prepared. As it was, some eight 10 g fractionations had to be performed to obtain even this minimum amount of test material. The composite of a single fraction thus available was just sufficient for the preparation of a single test dogbone and the determination of the "isocyanate equivalent" necessary to give an approximate optimum TDI level for the cure. This was the situation with two of the fractions selected for evaluation, namely, Fraction 2, representing essentially monofunctional polymer, and Fraction 9, representing a pure trifunctional PREP. With regard to the mid-fractions the close similarity of a number of them with regard to molecular weight and functionality allowed them to be combined so that the larger resulting sample could be used to prepare a wider variety of cures. Thus cures at two crosslinker levels were carried out and comparative tests run on original and reprecipitated samples of the combined Fractions 4, 5 and 6 (reprecipitation was used to clean up certain polymer fractions for analytical purposes as described on page 11; it was postulated not to have any significant effect on cure behavior).

(C) The cure formulations used and the resulting tensile data are summarized as part of Table 4. It will be seen that combined Fractions 4, 5 and 6, original (10469-149B and C) and precipitated (10469-150B and C) were essentially identical as predicted. A graphic illustration of the differences in cure behavior of the various fractions is given in Figure 10 where the performance of each is related to the same control, namely the parent PBEP 10001-186. It will be seen that the best results were achieved with Fraction 9 with an approximately 30% increase in tensile strength. On the other hand the increase in difunctional purity and the narrower molecular weight range of the mid-fractions 4, 5 and 6 has had little effect on tensile properties. In retrospect this latter result may not be too surprising in view of the improved performance noted with the all-trifunctional Fraction 9. Apparently the three functional groups are spread sufficiently far apart in the large (relative, that is, to the usual low molecular weight crosslinker) polymer molecules to avoid the formation of the hard crosslinked system that is the frequent result of all-trifunctional cures. The extremely poor result with Fraction 2 is in accord with the essentially monofunctional nature of this fraction.

(C) To summarize this portion of the work on the fractionation of PBEP and its precursors, PBEP was fractionated into 10 fractions ranging in molecular weight from 1500 to 11,000 and in functionality from <1 to 3. Tensile properties were shown to be improved by about 30% in the high molecular weight trifunctional polymer, to be essentially unchanged in the mid-fractions and to be greatly degraded in the monofunctional low molecular weight fraction. The mid-fractions proved to be the most thermally stable but the range of stability values proved to be relatively small. Approximate molecular weight distribution curves, both intergral and differential, were obtained for the polymer.

(C) Fractionation by Solvent Extraction

(C) In the work that has just been described PBEP was fractionated in a solvent gradient system using trichloroethane as solvent and carbon tetrachloride as the nonsolvent. However carbon tetrachloride was found to be a

CONFIDENTIAL

CONFIDENTIAL

Table 4. CURE STUDIES USING PBEP FRACTIONS

Cure No. 10469-	PBEP Source	PBEP, %w	Dibutyl Phthalate, %w	Catalyst, ^{a)} %w	Glycerol, %w (phr)	TDI, %w	(NH ₄) ₂ CO ₃ , %w	NOC Extr. (100 g) g/100 g	Cure		Drying Temp., °C	Extr. Time, min	Extr. Solvent, g
									Temp., °C	Time, min			
149A	Fraction 2 (precipitated)	27.92	22.24	0.50	0.56 (2)	3.54	43.14	1.00	70	1	70	1	1
149B	Fraction 4,5,6	28.09	22.66	0.51	0.56 (2)	2.95	43.47	1.00	70	1	70	1	1
149C	Fraction 4,5,6	27.79	22.20	0.50	0.83 (3)	3.67	43.14	1.00	70	1	70	1	1
150A	Fraction 4,5,6 (precipitated)	28.09	22.45	0.51	0.56 (2)	2.95	43.14	1.00	70	1	70	1	1
150B	Fraction 4,5,6 (precipitated)	27.80	22.20	0.50	0.83 (3)	3.67	43.14	1.00	70	1	70	1	1
150C	Fraction 9 (precipitated)	28.16	22.46	0.51	0.56 (2)	2.75	43.14	1.00	70	1	70	1	1
69A	Raffinate 10469-61-1	28.89	22.89	0.52	0.00 (0)	1.36	43.14	1.00	70	1	70	1	1
69B	Raffinate 10469-61-1	28.01	22.55	0.51	0.56 (2)	2.67	43.14	1.00	70	1	70	1	1
69C	Raffinate 10469-61-1	27.72	22.32	0.50	0.83 (3)	3.60	43.14	1.00	70	1	70	1	1
90A	Raffinate 10469-71-3	28.64	22.91	0.52	0.00 (0)	1.32	43.14	1.00	70	1	70	1	1
90B	Raffinate 10469-71-3	28.34	22.72	1.54	0.00 (0)	1.43	43.14	1.00	70	1	70	1	1
89A	Raffinate 10469-71-3	28.33	22.66	0.51	0.25 (1)	2.31	43.14	1.00	70	1	70	1	1
89B	Raffinate 10469-71-3	28.04	22.43	0.50	0.56 (2)	3.66	43.14	1.00	70	1	70	1	1
94A	Raffinate 10469-87-4	28.42	22.79	1.54	0.00 (0)	1.15	43.14	1.00	70	1	70	1	1
94B	Raffinate 10469-87-4	23.75	19.01	1.28	0.00 (0)	0.90	43.14	1.00	70	1	70	1	1
94C	Raffinate 10469-87-4	18.42	14.76	1.00	0.00 (0)	0.74	43.14	1.00	70	1	70	1	1
94D	Raffinate 10469-87-4	13.24	12.94	0.71	0.00 (0)	0.53	43.14	1.00	70	1	70	1	1
122A	Raffinate 10469-119-2	28.11	22.45	0.51	0.56 (2)	2.67	43.14	1.00	70	1	70	1	1
122B	Raffinate 10469-119-2	27.82	22.21	0.50	0.83 (3)	3.61	43.14	1.00	70	1	70	1	1
171A	Raffinate 10469-160-2	28.06	22.41	0.50	0.56 (2)	3.06	43.14	1.00	70	1	70	1	1
171B	Raffinate 10469-160-2	27.76	22.17	0.50	0.83 (3)	3.71	43.14	1.00	70	1	70	1	1
140A	10316-130 (ex PECH raff.)	28.68	22.90	0.52	0.00 (0)	1.46	43.14	1.00	70	1	70	1	1
140B	10316-129 (ex whole PECH)	28.69	22.89	0.52	0.00 (0)	1.48	43.14	1.00	70	1	70	1	1
141A	10316-130 (ex PECH raff.)	28.07	22.42	0.50	0.56 (2)	3.00	43.14	1.00	70	1	70	1	1
141B	10316-129 (ex whole PECH)	28.09	22.40	0.50	0.56 (2)	3.00	43.14	1.00	70	1	70	1	1
141C	10316-130 (ex PECH raff.)	27.78	22.19	0.50	0.83 (3)	3.73	43.14	1.00	70	1	70	1	1
141D	10316-129 (ex whole PECH)	27.80	22.17	0.50	0.83 (3)	3.73	43.14	1.00	70	1	70	1	1
156A	Raffinate ex 10316-130	28.77	22.98	0.52	0.00 (0)	1.16	43.14	1.00	70	1	70	1	1
156B	Raffinate ex 10316-129	28.76	22.99	0.52	0.00 (0)	1.16	43.14	1.00	70	1	70	1	1
156C	Raffinate ex 10316-130	28.16	22.50	0.51	0.56 (2)	2.69	43.14	1.00	70	1	70	1	1
156D	Raffinate ex 10316-129	28.15	22.51	0.51	0.56 (2)	2.69	43.14	1.00	70	1	70	1	1
156E	Raffinate ex 10316-130	27.86	22.26	0.50	0.84 (3)	3.43	43.14	1.00	70	1	70	1	1
156F	Raffinate ex 10316-129	27.85	22.27	0.50	0.84 (3)	3.43	43.14	1.00	70	1	70	1	1

a) Dibutyltin Diacetate.

b) Expressed as g/100 g PBEP but measured on the PBEP/PBEP mix.

AFRPL-TR-68-184
64599

CONFIDENTIAL

UNCLASSIFIED

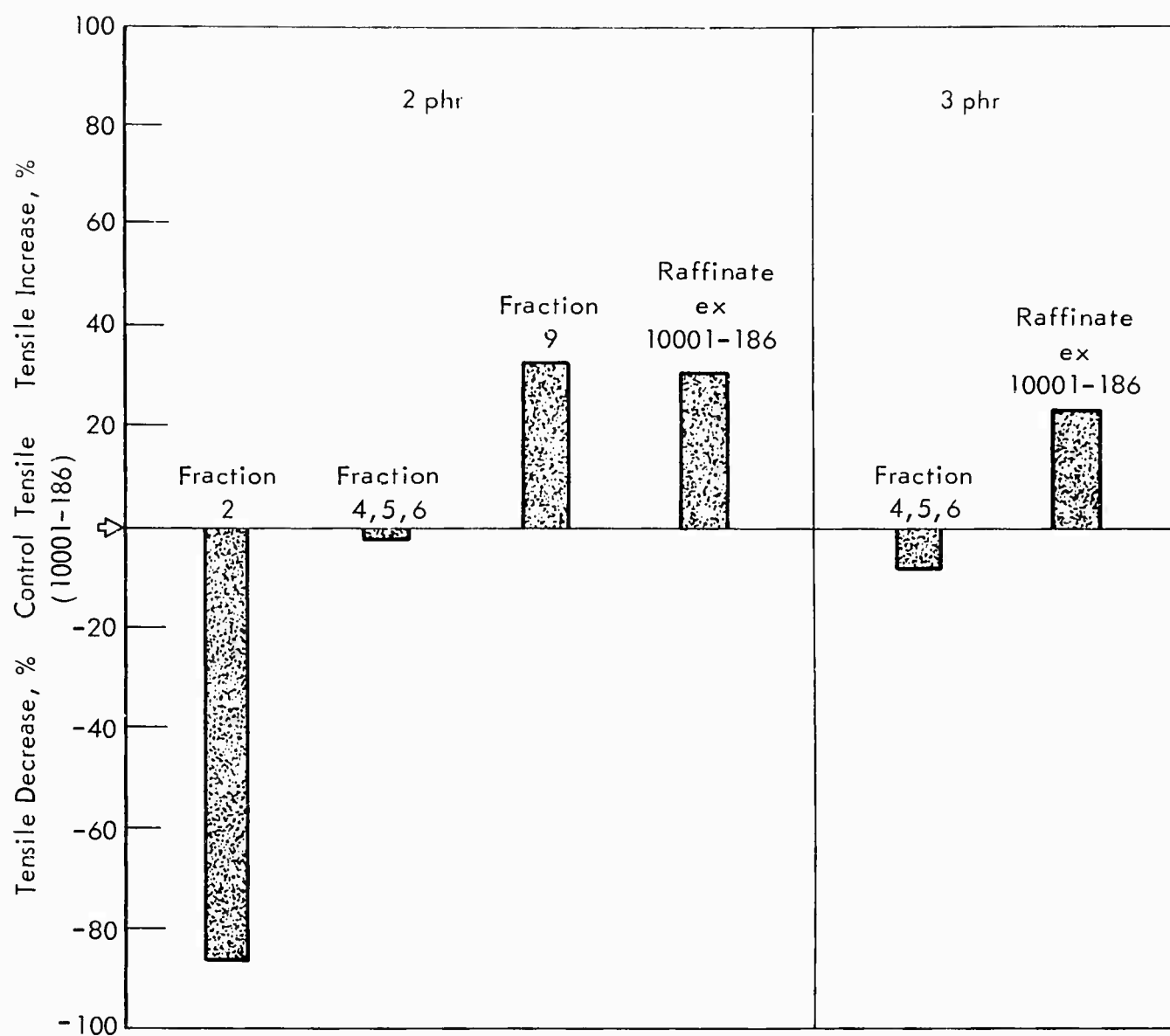


Figure 10. RELATIVE TENSILE PROPERTIES OF PBEP FRACTIONS

UNCLASSIFIED

CONFIDENTIAL

poor solvent rather than a nonsolvent with the result that the first PBEP fraction (10%) was extracted with CCl_4 alone. In order to evaluate further the possible use of CCl_4 extraction in a simplified and more practical fractionation system, PBEP was exhaustively extracted with CCl_4 . A lower molecular weight fraction consisting of 20-25% of the polymer proved to be soluble (Figure 11). The remaining polymer could then be readily eluted from the Chromosorb W column with methylene chloride (MDC). Provided the resulting two fractions have useful differences this procedure has many practical advantages over the above extended fractionation system including speed and the ability to produce larger quantities of material using similar sized equipment. A tabulation of the properties of a typical PBEP extract and raffinate and for comparison the original PBEP sample 10001-186 are given in Table 5. Significant differences are observed in the molecular weight and thermal stability and, most important, in the hydroxyl functionality.

(C) Table 5. COMPARISON OF PROPERTIES OF PBEP FRACTIONS

Properties	Extract	Raffinate	Original PBEP
C, %	27.7	26.1	24.5
H, %	3.3	2.9	3.5
N, %	15.3	15.9	15.8
NF ₂ , % (based on N)	56.7	58.9	58.7
F, %	40.1	43.0	40.5
F/N Ratio	1.94	2.0	1.89
Molecular Weight	1780	5950	3900
OH, eq/100 g	0.069	0.042	0.045
: functionality	1.2	2.5	1.8
Thermal Stability at 80°C, cc/g/100 hr	8.3	5.2	5.2

(C) The PBEP extract has a low hydroxyl functionality and a poorer thermal stability and hence is the less desirable or useful of the two fractions. However it was considered worthwhile to make a brief attempt at further fractionation of the material in order to obtain some idea of the range of molecular weights and hydroxyl functionalities present. Therefore a solvent gradient extraction was carried out on a small sample of the extract using the techniques and apparatus already described but with CCl_4 as the solvent and cyclohexane as the nonsolvent. Because of the limited size only four fractions were collected and only the analyses listed in Table 6 could be made. Nevertheless the data show that the extract contains material ranging in molecular weight from 500-3000 and with functionalities ranging from 0.3-1.6 (with the major portion ranging between 1 and 2 however). Subsequent work involving extractions of the whole polymer with cyclohexane and with petroleum

UNCLASSIFIED

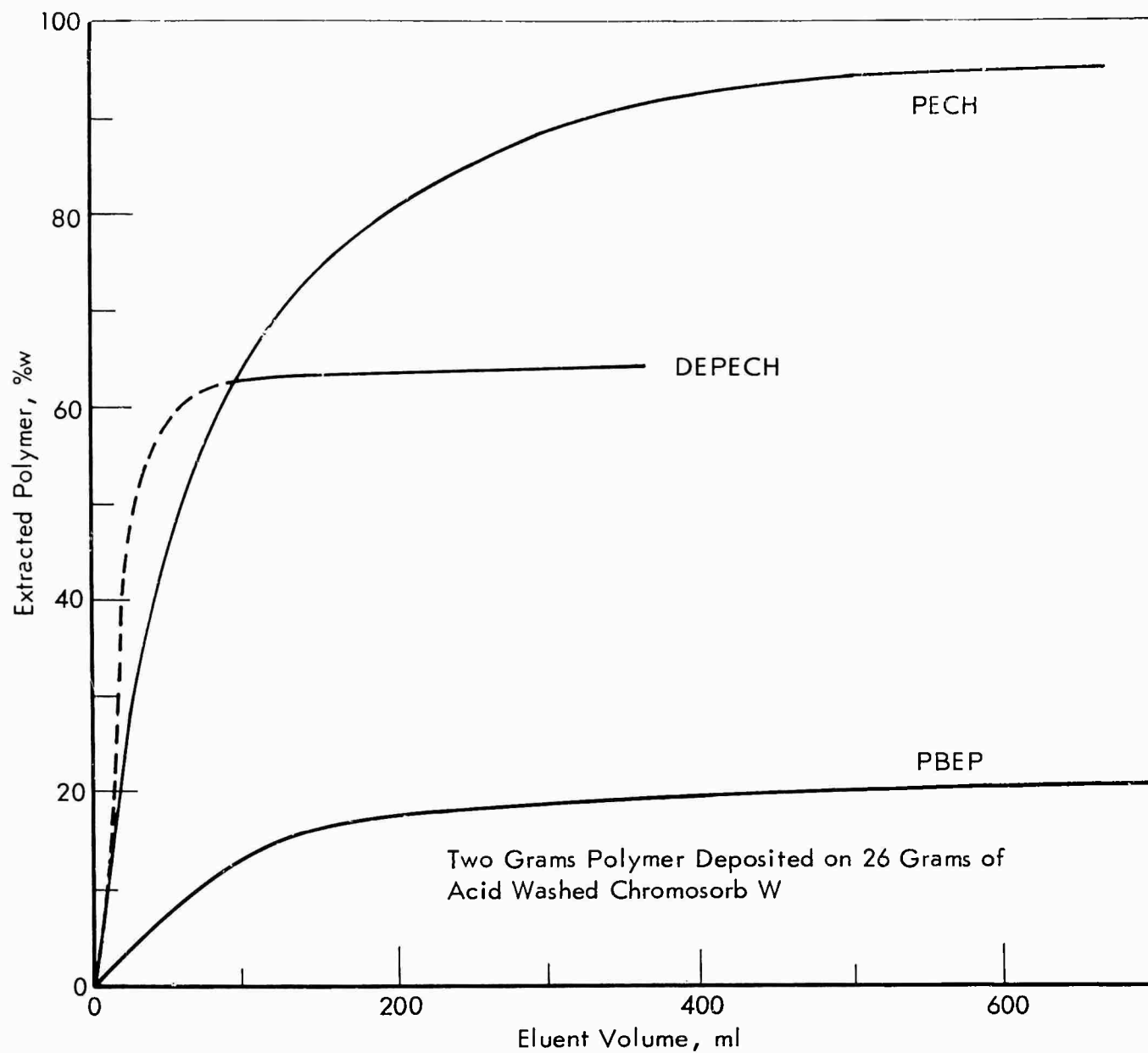


Figure 11. CARBON TETRACHLORIDE EXTRACTION OF PECH, DEPECH AND PBEP

UNCLASSIFIED

CONFIDENTIAL

ether, both of which remove approximately 1% of the polymer, has confirmed that even the lowest molecular weight fraction is essentially monofunctional; the very small amount of nonfunctional oil present is derived either from contaminants in the solvents themselves or from slight contamination present in the PBEP and introduced during the synthesis sequence, for example, from hydrocarbon lubricants used in reactor stirrer glands.

(C)

Table 6. FRACTIONATION OF PBEP EXTRACT

Fraction No.	Weight, %	Molecular Weight	Hydroxyl	
			eq/100 g	Functionality
1	4.5	570	0.053	0.3
2	33.2	1140	0.075	0.9
3	39.7	2060	0.078	1.6
4	23.6	2730	0.050	1.4

(C)

Evaluation of Raffinate Fraction

(C) The raffinate fraction, representing some 75% of the original PBEP, is of prime interest because of its greatly increased hydroxyl functionality. Due to the removal of the extract fraction containing a high proportion of monofunctional polymer a raffinate functionality as high as 2.5 is obtained compared with 1.8 for the whole polymer. The combined effect of the removal of a substantial proportion of monofunctional (and hence chain-terminating) polymer in the extract and the concomitant increase in the proportion of trifunctional (crosslinking) polymer was expected to lead to favorable changes in the cure behavior of the polymer. A tabulation of the cures carried out on various raffinate samples is included in Table 4. Graphic representation of some of the data and comparison with the performance of a regular PBEP sample 10001-186 are given in Figures 10 and 12. It will be seen that:

1. Raffinate PBEP may be cured without the addition of extra crosslinker, reflecting the increased proportion of trifunctional and reduced amount of monofunctional polymer. The rate of cure appears to be somewhat slower, requiring two to three days instead of the usual 1 day. This may be ascribed to the absence of added crosslinker (glycerol) with its faster reacting OH groups. Additional catalyst had some effect on reducing the cure time. Tensile properties are somewhat low. However it is felt that in a fully energetic system (which is known from work by United Technology Center to give much better properties with a regular PBEP than does our simulated (inert) system) the difference may not be so great and the properties may be adequate, especially where it is desirable to avoid energy losses by eliminating non-energetic crosslinker. The slower cure may have advantages of its own in that it may help to solve the short potlife problems which have plagued UTC in their

UNCLASSIFIED

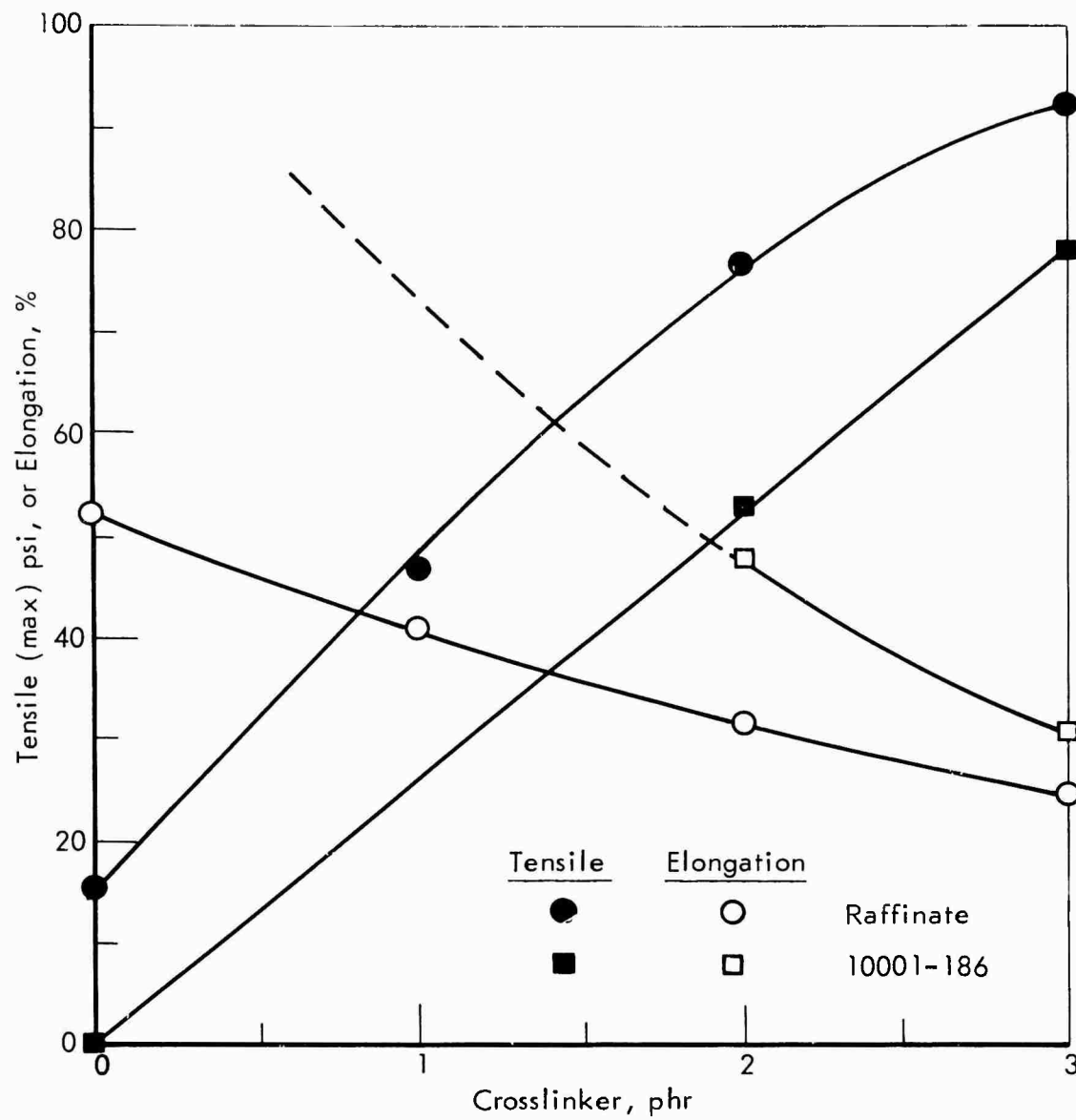


Figure 12. TENSILE PROPERTIES OF PBEP CURES WITH
(a) REGULAR PBEP AND (b) PBEP RAFFINATE

AFRPL-TR-68-184
64599

UNCLASSIFIED

CONFIDENTIAL

scale-up work. Similar benefits may spring from the related observation that the mix viscosity of the system is substantially lower and remains so during the entire mixing and pouring operation. The effect is strikingly illustrated in the cure series 94A, 94B, 94C and 94D in which hand mixes with solids loadings as high as 65% were successfully mixed and cast whereas the solids limit in similar mixes containing added crosslinker is about 45%. Apparently the major reason for the usual rapid increase in viscosity which limits potlife is the presence of the more rapidly reacting crosslinker.

2. At a given crosslinker level cured propellants containing raffinate PBEP have a higher tensile strength and lower elongation. The differences begin to decrease at the 3 phr crosslinker level where the influence of the added crosslinker begins to predominate. With regard to tensile strength the increase amounts to approximately 10-20 psi and remains fairly constant up to 3 phr crosslinker. Consequently the proportionate improvement is much greater at low crosslinker levels, e.g., 85% at 1 phr, 47% at 2 phr and 18% at 3 phr. The net result is that cures to a desired tensile strength may be achieved with either type of PBEP but with the regular PBEP requiring approximately twice the level of added crosslinker. A compensating feature is the considerably higher elongation achieved with the regular PBEP, although in all cases the elongations are in the satisfactory range of 30-60%.

(C) The Fractionation of PECH

(C) The fractionation work with PBEP described above has shown what differences might be expected when selected portions of the polymer are used as binders. However it is evident that this stage is the least desirable in which to discard any significant amount of the total polymer because of the high cost of the difluoramination step and the value of the resulting PBEP. Consequently in any practical scheme that is envisaged consideration will have to be given to the possibility of effecting the same or equivalent separation at an earlier stage in the synthesis. From this point of view PECH presents itself in the most favorable light since the unsaturated nature of DEPECH and its oxidative instability hints at many difficulties.

(C) In view of the limited time available and the fact that an exhaustive analytical-type of fractionation had already been conducted with PBEP it was decided to concentrate on achieving a separation comparable to the more practical carbon tetrachloride extraction of PBEP. The resulting PECH raffinate would then be evaluated by conversion to PBEP and comparison of the latter with regular PBEP and with PBEP raffinate.

(C) Fractionation by Solvent Extraction

(C) A brief survey of possible solvents showed PECH to be soluble in similar solvent systems to PBEP. However solubility in carbon tetrachloride, although incomplete, proved to be much greater than with PBEP, some 95% of the polymer being extracted (Figure 11). Solubility in cyclohexane was only 1-2%, comparable with PBEP. Using mixtures of CCl_4 and cyclohexane the curve shown in Figure 13 was constructed and used to select the solvent mixture necessary to extract a preselected amount of PECH. The mixture, 60% CCl_4 - 40%

UNCLASSIFIED

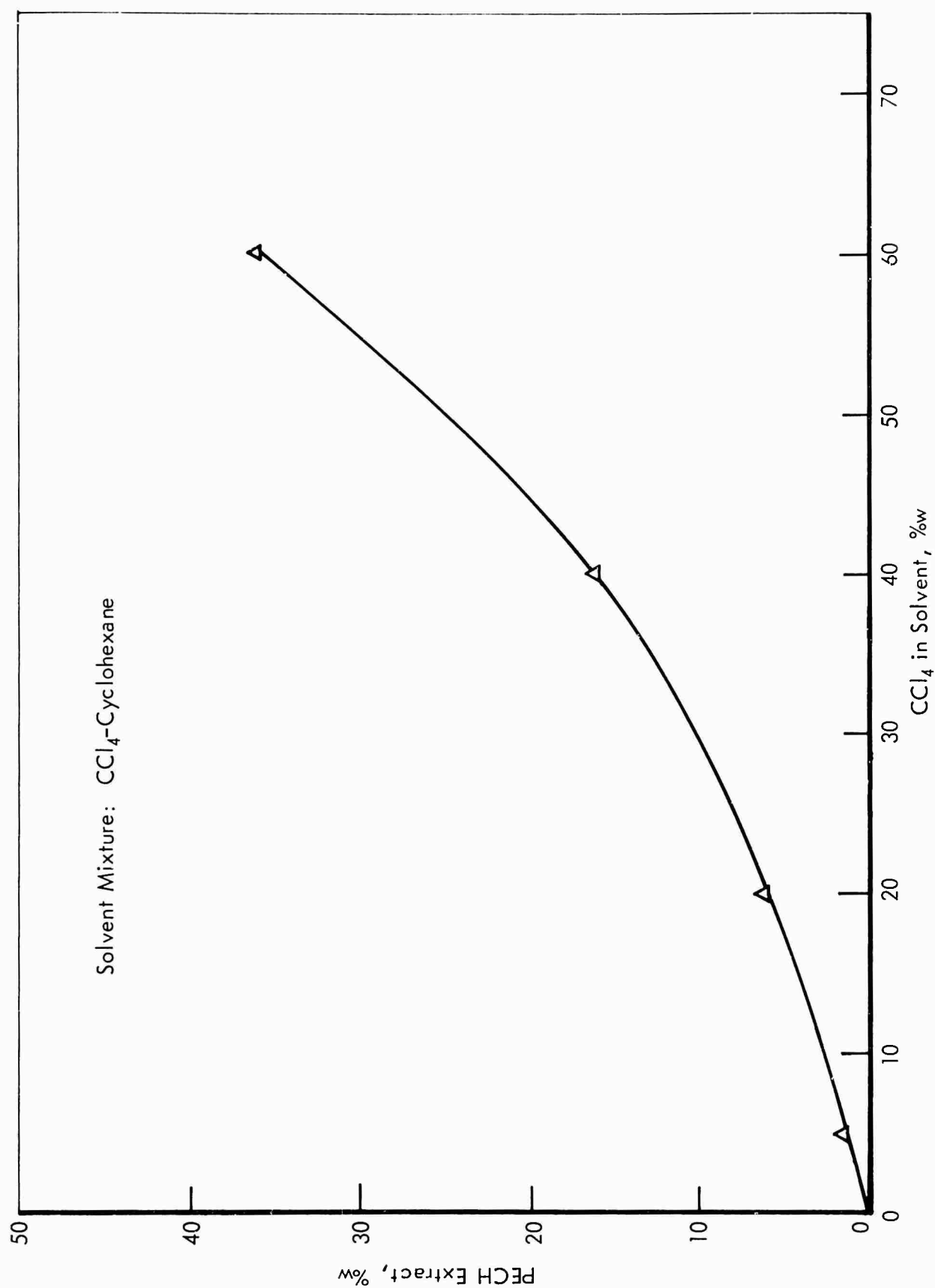


Figure 13. EFFECT OF SOLVENT COMPOSITION ON PECH EXTRACTION

AFRPL-TR-68-184
64264

UNCLASSIFIED

CONFIDENTIAL

cyclohexane, extracting approximately 35%, was chosen on the basis that by extracting to a level greater than the normal amount of extractables (~25%) found in PBEP no further quantity of extractable PBEP would be expected in a sample of PBEP made from the remaining PECH raffinate unless chain degradation occurred at some stage in the synthesis. Repeated extractions were made in order to prepare enough PECH raffinate for subsequent evaluation.

(C) A comparison of the properties of PECH extract and raffinate (Table 7) indicates the same differences as with PBEP, namely, low molecular weight and hydroxyl functionality in the extract and high molecular weight and functionality in the raffinate (the higher functionality of extract and raffinate compared with PBEP is directly attributable to the higher extraction of the PECH).

Table 7. PROPERTIES OF PECH FRACTIONS

Properties	Extract	Raffinate	Original PECH	
			Found	Based on Fractions
Fraction, %w	35.3	64.7	-	-
C, %w	39.2	38.8	39.0	-
H, %w	5.5	5.5	5.6	-
Cl, %w	36.9	37.1	37.0	-
Molecular Weight	1440	3690	2350	2380
OH, eq/100 g	0.111	0.074	0.081	0.087
functionality	1.6	2.7	1.9	2.1

(C) Evaluation of PECH Raffinate

(C) The raffinate was converted to DEPECH by dehydrochlorination with sodium methoxide in dimethyl sulfoxide solution at 50°C. The fact that the DEPECH had the expected theoretical molecular weight (2280) supports the contention that little or no degradation occurred during the dehydrochlorination step. Functionality also remained high. Difluoramination of the DEPECH under batch conditions at 90°C was conducted in the usual way and the product isolated for evaluation. For comparison purposes a sample of the whole PECH was dehydrochlorinated and converted to PBEP in a parallel series of experiments. Table 8 summarizes the analytical data for both series. Significant observations include the following:

1. Despite the removal of some 35% extractables at the PECH stage the PBEP made from the PECH raffinate still contained 13% low molecular weight extractable material. The appearance of this polymer is strong evidence for the occurrence of chain scission during the difluoramination reaction.

CONFIDENTIAL

Table 8. EVALUATION OF PECH RAFFINATE

Properties	Raffinate Series	Whole PECH Series		
<u>PECH</u>				
C, %w	38.8	39.0		
H, %w	5.5	5.6		
Cl, %w	37.1	37.0		
Mol Wt	3690	2350		
OH, eq/100 g	0.074	0.081		
Functionality	2.7	1.9		
<u>DEPECH</u>				
Mol Wt	2280	1740		
OH, eq/100 g	0.136	0.11		
Functionality	3.0	1.9		
Unsaturation, moles/100 g	1.40	1.32		
<u>PBEP</u>				
C, %w	26.0	26.2		
H, %w	2.9	2.9		
N, %w	15.9	15.9		
NF ₂ , %w (based on N)	59.1	59.1		
F, %w	39.8	38.9		
F/N	1.84	1.80		
Mol Wt	~4000	3570		
OH, eq/100 g	0.040	0.047		
Functionality	~1.6	1.7		
Thermal Stability at 80°C, cc/g/100 hrs	4.2	4.5		
CCl ₄ Extractables, %w	12.9	25.2		
<u>CCl₄ Extraction</u>	<u>Raffinate</u>	<u>Extract</u>	<u>Raffinate</u>	<u>Extract</u>
C, %w	27.2	29.0	26.8	27.5
H, %w	2.8	3.1	3.1	3.1
N, %w	15.8	15.5	15.3	15.2
NF ₂ , %w (based on N)	58.6	57.4	56.7	56.4
F, %w	41.0	37.1	40.0	38.0
F/N	1.92	1.77	1.93	1.85
Mol Wt	5180	1210	5500	1620
OH, eq/100 g	0.037	0.059	0.040	0.064
Functionality	1.9	0.7	2.1	1.0
Thermal Stability of 80°C, cc/g/100 hrs	4.7	-	4.0	-

CONFIDENTIAL

2. Further evidence for chain degradation is the low molecular weight of the PBEP. Although a range of values was obtained the average molecular weight was approximately 4000, much lower than the expected 5200, based on the DEPECH molecular weight.

3. The substantial loss of hydroxyl functionality (dropping from 2.7 or greater in the PECH and DEPECH to ~1.6 in the PBEP) is not unexpected if chain scission is taking place, since trifunctional chains would be converted to mixtures of di and monofunctional chains, and difunctional chains would be converted to monofunctional.

4. An additional feature of the hydroxyl changes, however, is the apparent and unexpected loss of hydroxyl content. If no hydroxyl groups had been destroyed during the difluoramination it is estimated that the hydroxyl content would have been 0.060 eq/100 g compared with the actual value of 0.040 eq/100 g. It should be noted that this hydroxyl loss was not observed in the whole PECH series (calculated value, 0.049 eq/100 g versus found, 0.047 eq/100 g) and therefore is of concern only if PECH raffinate is being considered as a starting point for PBEP.

(C) While it is relatively easy to understand the reasons for chain scission, namely, breakdown of the vinylidene ether linkages in unreacted DEPECH catalyzed by HF generated from NF_2 groups already added to the unsaturated polymer, it is more difficult to envisage the reasons for the actual loss of hydroxyl groups, especially since an apparent distinction exists here between the whole polymer and the PECH raffinate-derived fraction. Therefore it is considered very desirable that at the first opportunity the reaction sequence leading to the hydroxyl loss be rechecked.

(C) 5. Loss of HF as evidenced by relatively low F/N ratios is apparently greater in both the raffinate and whole PECH series than in an average PBEP. (Since HF is postulated to be a factor in the chain degradation mentioned above this could mean that said degradation may be unusually great in the present test series.) It is noteworthy that upon extraction of the PBEP from both series it was found that the polymer with low F/N had accumulated in the extract. This may be interpreted to mean that loss of HF took place preferentially from the lower molecular weight polymer but a more likely explanation is that the polymer is low molecular weight because HF evolution took place from it; that is, the evolving HF incited chain scission preferentially at nearby bonds with the formation of lower molecular weight polymer with a relatively low F/N ratio.

(C) As the final step in the evaluation of the PECH raffinate, cure studies were made at 0 phr, 2 phr and 3 phr crosslinker levels on a) the original PBEP samples (both series) and b) the raffinate PBEP samples derived from them. The cure formulations used and the tensile properties of the test dogbones are included in Table 4 (Cure Nos. 10469-140A to 10469-156F) and part of the data are presented graphically in Figure 14. It will be seen that.

1. At zero crosslinker level no cure was obtained with either the PBEP from the PECH raffinate or the control sample. While this is not unexpected behavior for the control sample a cure would be expected from the

CONFIDENTIAL

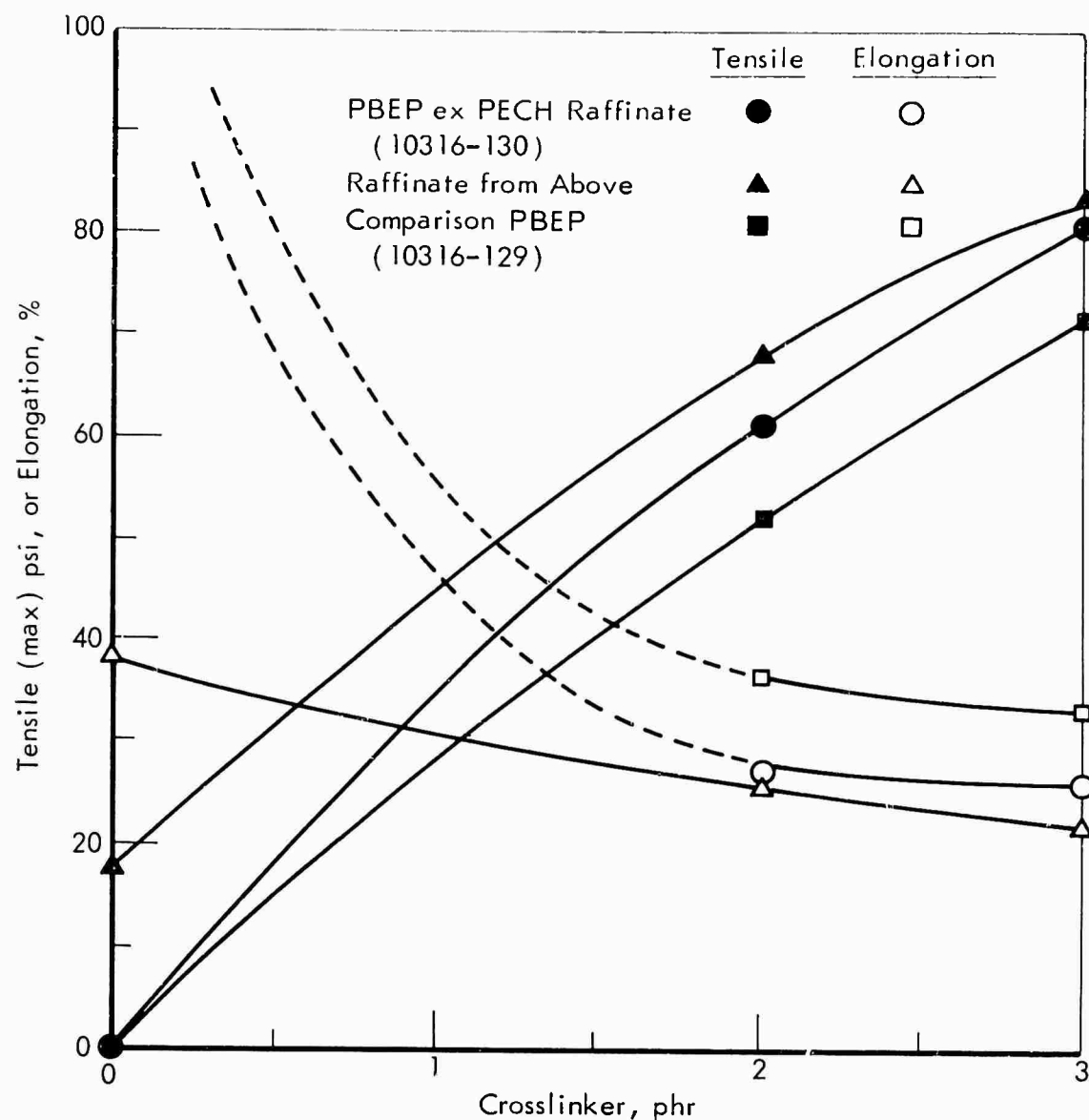


Figure 14. TENSILE PROPERTIES OF PBEP FROM PECH RAFFINATE

AFRPL-TR-68-184
64599

CONFIDENTIAL

CONFIDENTIAL

raffinate-derived sample unless degradation had resulted in the formation of further quantities of lower molecular weight monofunctional polymer. Note moreover that normal curability for both samples at 0 phr crosslinker was found after CCl_4 extraction of the PBEPs (Cure Nos. 10469-156A and B) had removed the monofunctional lows.

2. Tensile strength of the raffinate-derived PBEP was somewhat higher than the control (at levels above 0 phr crosslinker) but the improvement is considerably less than was observed in the earlier series of experiments where the low molecular weight fraction was removed at the PBEP stage (Figure 12).

3. The improvement in the tensile strength of the PBEP "raffinate" obtained by solvent extraction of the PECH raffinate-derived PBEP approximated that in the earlier test series (Figure 12).

(C) Thus it is evident that the results of these cure tests confirm and amplify the earlier conclusions, based on analyses of PECH raffinate and derived DEPECH and PBEP. In summary these conclusions were that PBEP made from a PECH raffinate did show some improved properties. However, these improvements were minimized by the occurrence of chain degradation and possibly the loss of some hydroxyl groups during the difluoramination step.

(C) The Fractionation of DEPECH

(C) The fractionation of the polymer at the DEPECH stage is an alternative, potentially practical approach to the upgrading of PBEP which may have certain handling advantages, relative to PECH, due to the solid nature of this polymer. Moreover DEPECH was found to be much more rapidly solvent-extracted than either PECH or PBEP. As shown in Figure 11 complete extraction was effected using only 1/4 to 1/6 of the solvent required with the other polymers. For these and other reasons it was desirable to investigate the possibility of fractionating the polymer at this stage.

(C) Small scale tests established that DEPECH could be deposited on Chromosorb W packing from methylene chloride solution and quantitatively recovered by elution with the same solvent. Extraction tests with CCl_4 gave a value of approximately 60% extractables, placing DEPECH between PBEP (25%) and PECH (95%) (Figure 11). Cyclohexane extracted about 6%, substantially more than with either PBEP or PECH but still insufficient for our purpose. However the same mixture of 60%v CCl_4 - 40%v cyclohexane used to extract PECH proved to be suitable, extracting approximately 30% of the polymer. Quantitative recovery from the column of the remaining DEPECH (raffinate) could be carried out with a number of solvents including methylene chloride, dioxane and tetrahydrofuran. (It is interesting to note that this could not be done with acetone, the solvent used in the difluoramination of DEPECH; a subsequent acetone extraction test confirmed that approximately 1/3 of the DEPECH (higher molecular weight fraction) was insoluble in cold acetone and dissolved in hot acetone only to form a gel on cooling). Unfortunately little progress was made beyond this point in the short time available, due to the instability of the recovered fractions. This sensitivity is undoubtedly due to the unsaturation

CONFIDENTIAL

in the polymer, the more so as it is in the form of vinylidene ether groups. As a result substantial amounts (50-75%) of unsaturation were lost shortly after recovery of the fractions. More unexpectedly there were indications of a loss of hydroxyl content. Efforts to combat the instability have included the extensive use of inhibitor (hydroquinone) in contact with the polymer at all times on and off the column, immediate bicarbonate treatment of the effluent (methylene chloride elution) to remove any acidity and the use of alternative eluting solvents. While a considerable reduction in the unsaturation loss was possible the successful isolation of completely stable DEPECH fractions had not been achieved at the time it was decided to discontinue this part of the work.

(C) Carbon Treatment of PBEP

(C) The effect of carbon treatment on the properties of PBEP has been described in an earlier report.^{a)} The data showed that a substantial improvement in the thermal stability of the polymer could be achieved, values as low as 1.5 cc/g/100 hr after 200 hr at 80°C being obtained after up to 12 carbon treatments of the PBEP in dilute methylene chloride solution. However the treatment also caused the loss of part of the fluorine which in the most severe case amounted to some 18% of the total or approximately one-third of the primary NF₂ groups. Presumably the improvement in thermal stability is due to the loss of these less stable groups.

(C) Subsequent work with different PBEP samples and carbon from a different source has confirmed the improvement in thermal stability and the loss of a portion of the fluorine. However the apparent loss of fluorine proved to be considerably less than in the earlier series of tests. The pertinent data are given in Table 9. The data indicate that a relatively small proportion of the NF₂ groups are responsible for a major part of the thermal instability in the polymer and that therefore it is not necessary to remove a large number of the energetic groups to procure a significant improvement in stability. Moreover the loss of a small amount of NF₂ may not be unacceptable since conversion to the more stable but still favorable nitrile group will have a relatively small effect on the specific impulse of PBEP propellants.

(C) Recently, encouraging indications that the carbon treatment of PBEP may eliminate or reduce its catalyst-deactivating tendencies have further increased the interest in this procedure. Details of this work are included in a later section of this report.

a) Shell Special Technical Report AFRPL-TR-68-82, May 1968, Contract No. AF04(611)-11645, page 12.

CONFIDENTIAL

Table 9. EFFECT OF CARBON TREATMENT ON PBEP - 2nd SERIES

Sample No. 10469-	No. of C Treatments	Product Properties					
		Thermal Stability at 30°C, cc/g/100 hr	N, %w	F, %w	F/N	Molecular Weight ^{a)}	OH Functionality ^{b)}
163-4	2	4.9 ^{c)}	16.3	41.4	1.87	3500	1.8
163-5	5	3.4	15.8	40.3	1.88	3360	1.7
163-6	10	2.7	16.8	39.8	1.74	3250	1.8

a) Molecular Weight determined by Vapor Pressure Osmometer.

b) Hydroxyl content used to estimate functionality was determined by an infrared technique using poly(propylene glycol) as calibration standard.

c) Original (untreated) PBEP had a thermal stability value of 5.5 cc/g/100 hr.

(C) PBEP Curing Studies

(C) A procedure for carrying out small scale reactions between TDI and various coreactants, present or likely to be present in the PBEP curing system, has been developed. The reactions are monitored for TDI consumption by an infrared technique. Among the reactions which have been surveyed and compared are those between TDI and PBEP, TDI and glycerol, and TDI and water, in all cases both under catalysis and in the absence of catalysts. Details of the procedure and the results have already been reported.^{a)} Briefly, in the catalyzed systems TDI was found to react rapidly with all three of the above reactants. With due respect to the roughness of the data the order of activity at 50% conversion appeared to be H₂O > PBEP > glycerol. This order is reversed however with regard to PBEP and glycerol at higher conversions (60%) suggesting that there may be a proportion of the OH groups in PBEP which are considerably less reactive in the isocyanate reaction. In general there appear to be no gross (order of magnitude) differences in the reactivity of these potential ingredients with TDI in the PBEP curing system. In uncatalyzed systems the PBEP-TDI reaction appeared to take a different course from the autocatalytic behavior of the water-TDI and glycerol-TDI reactions. Approximately 20-30% of the TDI was consumed with some rapidity and then reaction virtually stopped. This suggested the presence in PBEP of a small amount of a species more reactive toward TDI than the OH groups in water, glycerol or PBEP. HF would appear to be a likely candidate for this role since halogen acids are known to react uncatalyzed with isocyanates to form carbamoyl halides. Based on the amount of TDI consumed it was estimated that only about 1% of the total PBEP fluorine was involved in the reaction.

a) Shell Special Technical Report AFRPL-TR-68-82, May 1968, Contract No. AF04(611)-11645, page 17ff.

CONFIDENTIAL

(C) United Technology Center has been experiencing problems in obtaining reproducible cures when attempting to scale-up propellant mixes to the 1-4 lb level. This has been attributed to partial deactivation of the catalyst, dibutyltin diacetate (DBTDA), at the low levels found by UTC to be necessary for adequate potlife. Once more HF has been suggested as a participant, this time in the deactivation reaction. In an effort to extend our knowledge of this postulated deactivation reaction our cure studies were extended to include the effect of varying catalyst levels on TDI conversion. A graphic depiction of the results is given in Figure 15 (the complete details were given in the earlier report).^{a)} The deactivation effect on the catalyst as a result of contacting it for 4.5 hr with PBEP is also shown in Figure 15 by the solid (black) data points. It will be seen that:

1. At the 0.25% catalyst level deactivation has reduced the activity of the catalyst to the equivalent of 0.065% catalyst, i.e., a loss of approximately 75%.

2. At the 1% level the absolute loss of activity is roughly the same and therefore the effect on TDI consumption is negligible. Unfortunately at this higher catalyst level potlife problems are experienced by UTC.

(C) Further work has now been done both to a) recheck the earlier findings and b) determine whether the catalyst deactivating effect can be reduced by a suitable treatment of the PBEP. With regard to a) excellent agreement was obtained with the earlier data confirming the deactivating effect of the PBEP as is shown in Figure 16. Efforts to moderate the deactivating influence of the PBEP have shown (Figure 17) that a sample of the PBEP raffinate behaved similarly to the whole polymer with regard to the extent of deactivation. However the TDI consumption curve indicated a somewhat lower reaction rate at a given catalyst level. Such behavior might be anticipated from the lower hydroxyl content of this higher molecular weight PBEP fraction and may be of some practical value in extending the potlife of propellant mixes.

(C) Of considerably greater significance were the results obtained with a PBEP sample which had been treated 10 times with carbon. These results are shown graphically in Figure 18 and may be summarized as follows:

1. No deactivation of the catalyst took place during 4.5 hr contact time with the PBEP at 50°C. This was confirmed in duplicate tests.

2. The effect of catalyst concentration on the rate of TDI consumption was much greater than with the regular polymer. Taken together these two results would appear to allow for considerably better control over the potlife and cure rate of propellant mixes.

(C) Since it is known from analyses of the carbon-treated PBEP samples that a portion of the more labile fluorine atoms from the primary NF_2 groups are removed by this treatment it would appear that these are the same fluorine atoms responsible for the catalyst deactivating action of PBEP. Just how much

a) Shell Special Technical Report AFRPL-TR-68-82, May 1968, Contract No. AF04(611)-11645, page 19.

CONFIDENTIAL

CONFIDENTIAL

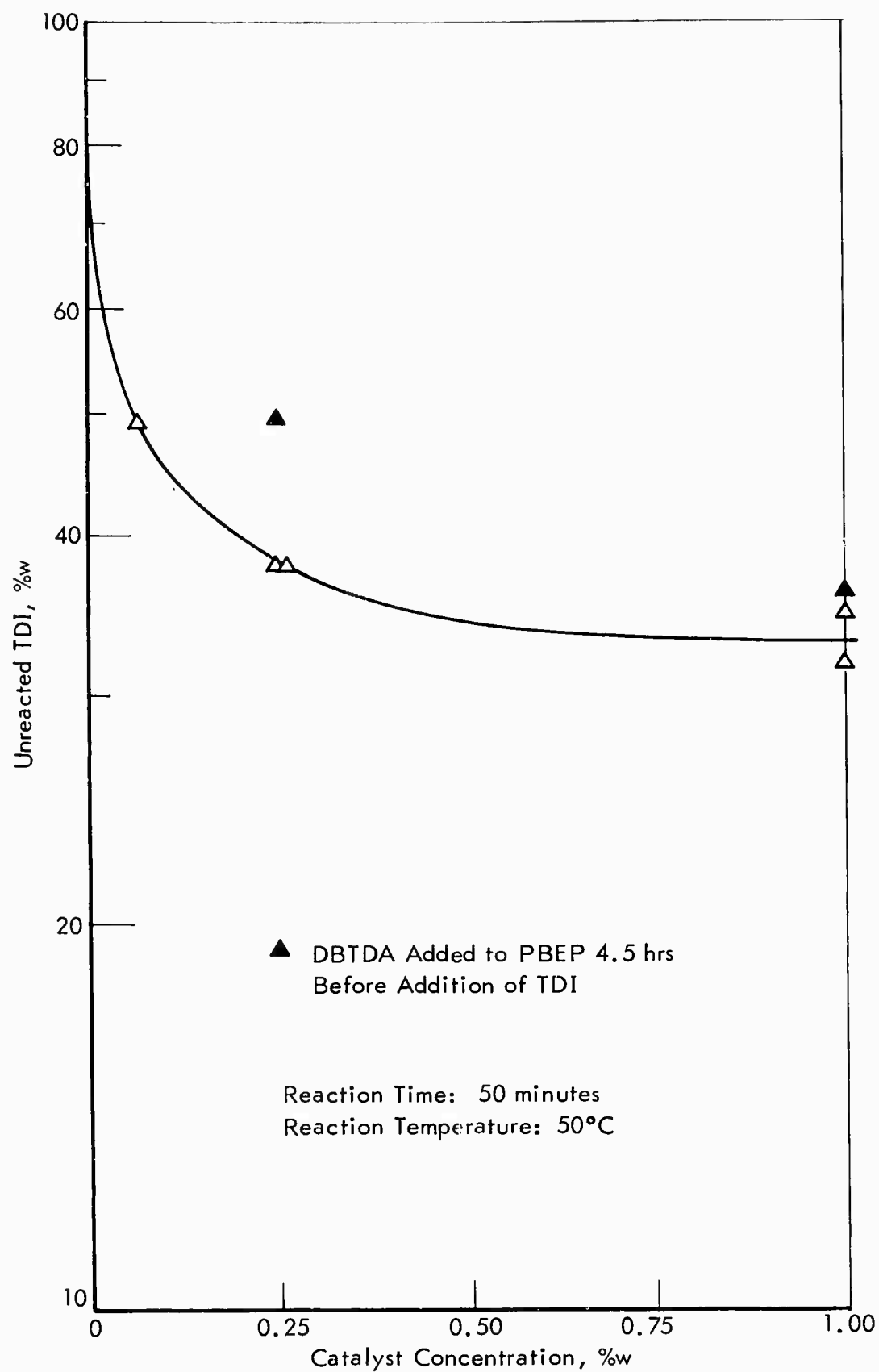


Figure 15. EFFECT OF DIBUTYLTIN DIACETATE CONCENTRATION ON TDI-PBEP REACTION

AFRPL-TR-68-184
64599

CONFIDENTIAL

CONFIDENTIAL

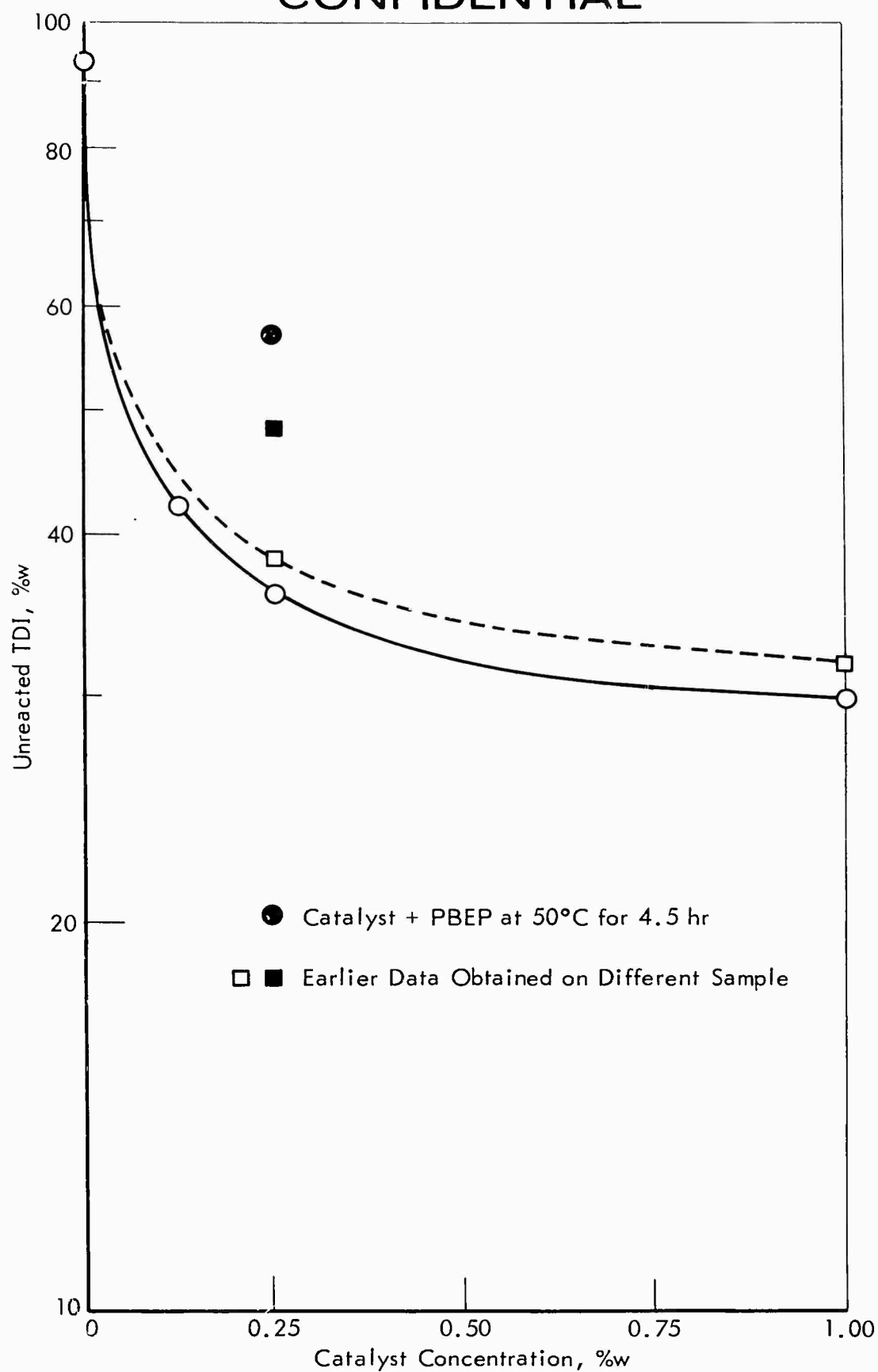


Figure 16. DEACTIVATION OF DBTDA BY PBEP

AFRPL-TR-68-184
64599

CONFIDENTIAL

CONFIDENTIAL

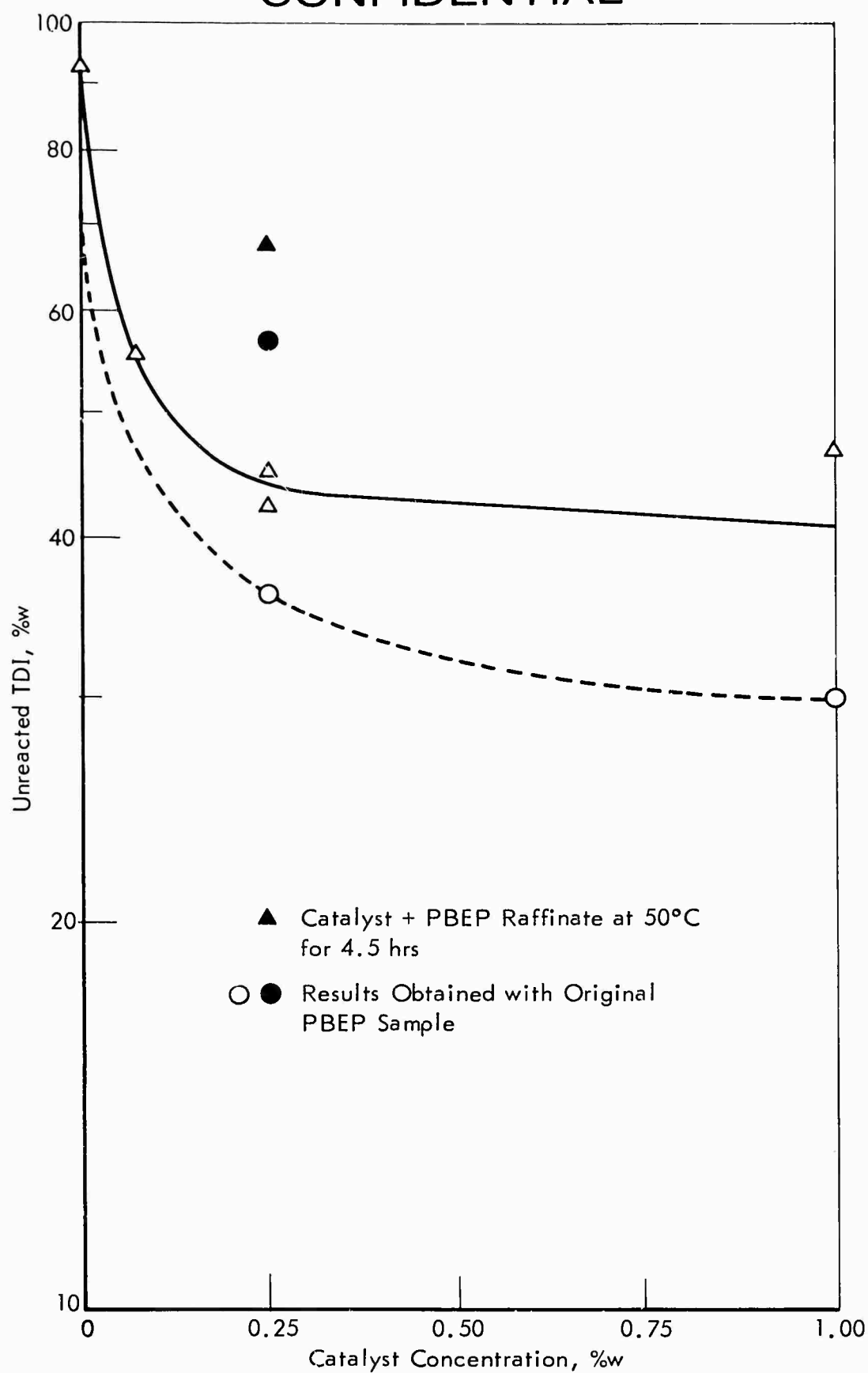


Figure 17. EFFECT OF PBEP RAFFINATE ON
DEACTIVATION OF DBTDA

CONFIDENTIAL

CONFIDENTIAL

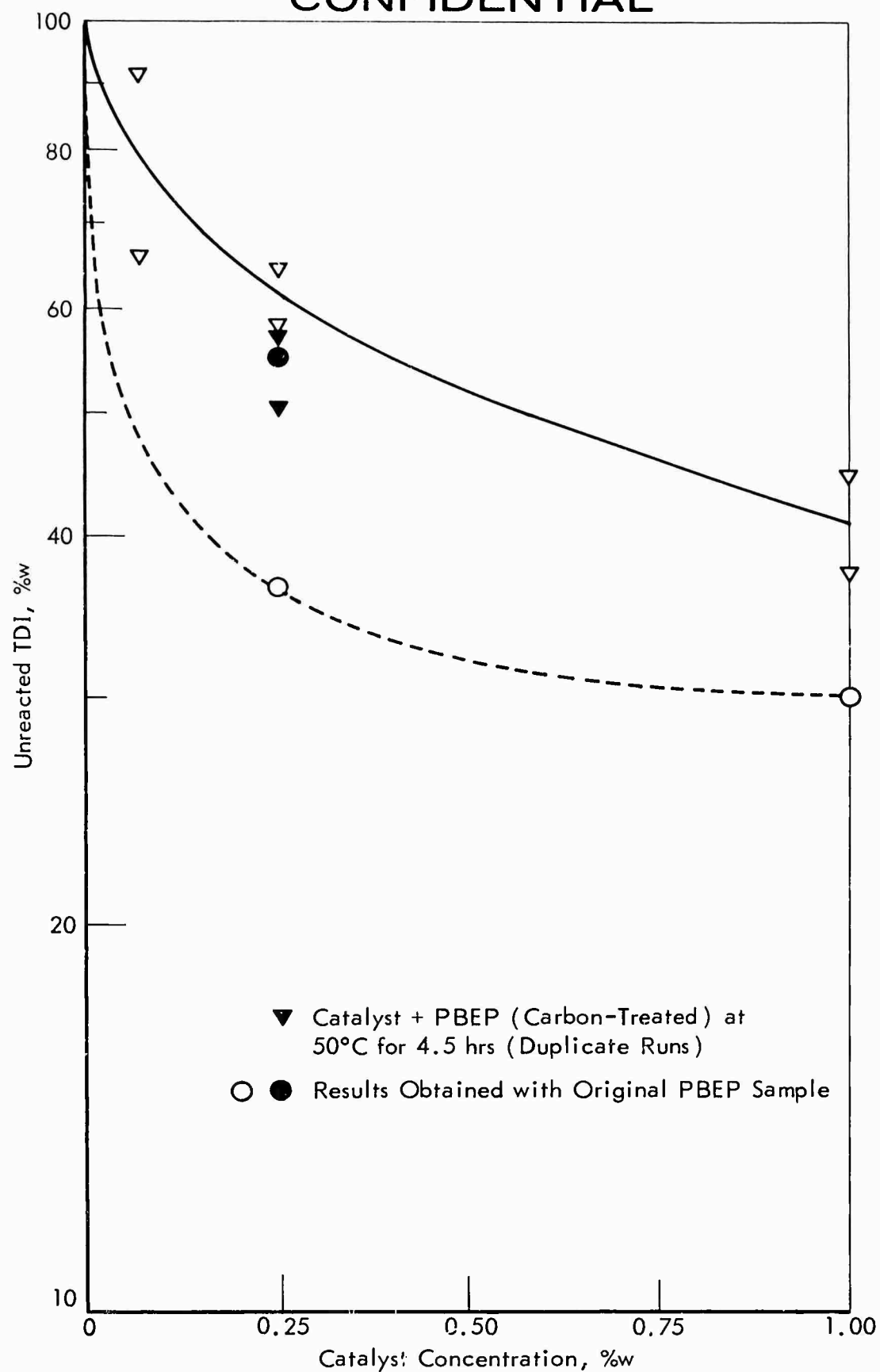


Figure 18. EFFECT OF CARBON-TREATED PBEP ON DEACTIVATION OF DBTDA

AFRPL-TR-68-184
64599

CONFIDENTIAL

CONFIDENTIAL

of this labile fluorine it is necessary to remove to prevent deactivation is not known at present. However it is very encouraging to note that this effect has been observed in a PBEP sample from the second series of carbon treatments in which considerably less fluorine (<5%) was removed compared with the original series (~18%).

(C) Stability of PBEP Solutions

(C) In order to clarify the position with regard to the stability of PBEP in solution under conditions comparable with those normally used for storing or shipping the polymer a series of tests was conducted at temperatures ranging from -10 to -20°C for 8 months to +50°C for 4 weeks. The PBEP solutions (in methylene or ethylene dichloride) were stored both in glass and in polyethylene containers. In addition to the normal treatment (MDC solution water-washed and dried over $MgSO_4$) samples were dried and stored over Molecular Sieves or had additional water added to them (to two different levels). Key analyses were run on the polymers before and after the storage period and have already been reported in detail in our earlier report.^{a)} It was concluded that there had been no significant change in the properties of the PBEP polymer under any of the conditions of storage.

(C) Large Scale Preparation of PECH and DEPECH^{b)}

(C) As a source of starting material for the PBEP production runs large scale preparations of PECH and DEPECH were carried out by procedures described earlier.^{c)} One 200-pound polymerization of epichlorohydrin was completed and the dehydrochlorination step to give DEPECH was performed five times to yield from 9 to 21 pounds of product per batch. All products were analyzed and tested for PBEP preparation and found satisfactory.^{d)}

(C) Addition of N_2F_4 to DEPECH

(C) One phase of the present project was to construct a unit for the continuous preparation of PBEP, and to carry out a certain amount of process optimization work which would develop conditions to assure the production of material which would be at least comparable in quality to the material which had been produced previously by the batch process. In the current work good product was defined as that which possessed good thermal stability. It has always been found that products of high thermal stability also always possessed the maximum in NF_2 content. The continuous product which has been prepared has been shown to have hydroxyl functionality, molecular weight, and curing characteristics comparable to that found in the past on batch product.

-
- a) Shell Special Technical Report AFRPL-TR-68-82, May 1968, Contract No. AF04(611)-11645, page 13.
 - b) The large scale preparations were carried out by A. C. Mueller in the Experimental Plants Department.
 - c) Shell Final Report AFRPL-TR-67-151, Contract No. AF04(611)-11412, March 1966-February 1967.
 - d) Shell Special Technical Report AFRPL-TR-68-86, Contract No. AF04(611)-11645, May 1968.

CONFIDENTIAL

(C) Process Equipment Description

(C) The unit used for studies on the continuous process for PPEP is shown schematically in Figure 19. A solution of DEPECH in acetone (1) is metered to a 50 cc stirred, temperature controlled mixer (2) to which N_2F_4 (3) is added at a constant controlled rate via a two-stage Lapp compressor CPD-1AP-1 with closed loop stroke control on the first stage. From this mixer the solution is passed through two 75 ft by 0.18 inch ID stainless steel coil reactors in series (4,5) each with independent temperature control obtained by instrumented mixing of steam and water. Cold water is added at a constant rate to the jacket of the second stage reactor, and steam is mixed with this in a controlled manner to achieve the desired temperature. The exit stream from this jacket of the second stage then enters the jacket of the first stage after having cold water added to it in a controlled manner such that the desired temperature in the first stage is obtained. After the reaction is completed, the solution is cooled to 15-20°C by passing through a water jacketed section and the pressure is reduced from reaction conditions (300-400 psig) to atmospheric pressure as it passes through a pair of Grove regulators (6,7). Excess N_2F_4 is removed by a countercurrent nitrogen stream as the solution passes through a two-inch ASCO-50 Rotafilm Evaporator (8) operating at ambient temperature. The effluent is diluted with methylene chloride (9) and extracted with water (10) in a Podbielniak Model 5000 centrifugal extractor (11). The acetone-free product stream (12) from this unit is dried by passage over 13-X Linde molecular sieves (13) and then treated to remove unstable trace contaminants by passage over 28-200 mesh silica gel (14). The final product (15) is obtained as a dry, acetone-free, methylene chloride solution.

(C) Product Quality Criteria

(C) To develop the process for the preparation of optimum quality product the prime goal was the achievement of near quantitative saturation of the double bonds in DEPECH with N_2F_4 . As a direct check on the extent of difluoramination an infrared spectrum of the product was recorded and the presence of a shoulder or band at 6.05 μ was taken to be an indication that the reaction had stopped considerably short of completion. As a finer measure of degree of difluoramination the thermal stability of the product was measured. This measurement^{a)} required at least 72 hours for a significant indication of the final result and 200 hours before the test would be completed in the prescribed manner. The ultimate in thermal stability obtainable with currently prepared PPEP is about 5-6 cc/g/100 hr at 80°C so that experimental conditions which gave thermal stabilities in the range of 4-7 cc/g/100 hr. were taken to be near the optimum. It was observed that an extrapolation of several thermal stability readings taken during the first 72 hours allowed a fairly good estimate of the final measured thermal stability after 200 hours. It was also observed that the thermal stability measured on rather freshly prepared product, i.e., 24-48 hours old, was generally about 1-1.5 units greater than would be found on the same product after it had been aged for approximately five to seven days.

a) Shell Final Report S-13881, Contract No. AF 04(611)-8168, April 1, 1962-March 31, 1963.

CONFIDENTIAL

CONFIDENTIAL

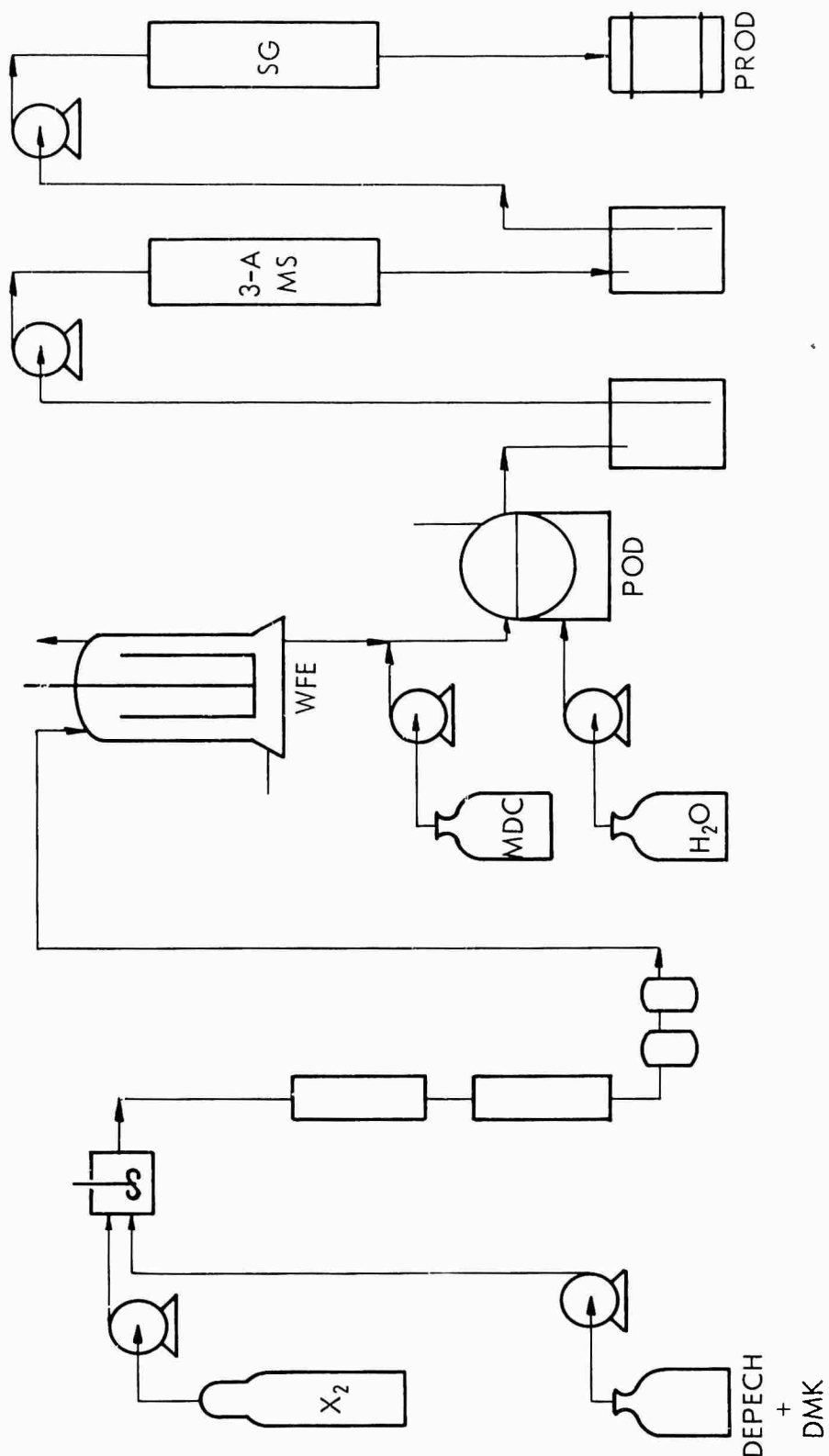


Figure 19. SCHEMATIC FLOW DIAGRAM OF CONTINUOUS PBEP UNIT

AFR PL-TR-68-184
62965

CONFIDENTIAL

CONFIDENTIAL

(C) As work progressed it appeared that certain treatment of DEPECH prior to reaction with N_2F_4 was responsible for the development of nitrile groups in PBEP. The existence of this nitrile group was observed by the presence of an infrared absorption band at 4.47μ . This is located in a region normally virtually free of absorption in the IR spectrum for PBEP samples. It is of interest to note that the dehydrofluorination reaction which produced this nitrile group apparently did not bring about at the same time any degradation of the product which would have been expected under the reaction conditions.

(C) Process Variables Studied With Continuous PBEP Unit

(C) Table 10 summarizes the more important runs carried out on the project to determine the near optimum conditions for the continuous preparation of PBEP.

Table 10. REACTION CONDITIONS EMPLOYED IN CONTINUOUS
PBEP UNIT AND THERMAL STABILITY OF PRODUCTS

Run No.	Total Residence Time, hr ^a)	Excess N_2F_4 , ^b) %	Reactor Temp, °C		Thermal Stability ^c)
			First Stage	Second Stage	
1	1-1/2	20	60	90	14
2	1-1/2	40	60	90	8
3	1	150	60	90	7
4	2	40	60	90	8
5	1-1/2	40	60	90	8
6	1	40	60	90	7
7	2/3	40	60	90	12
8	1	40	60	100	6
9	1	40	60	110	7
10	2	40	60	110	7
11	1	40	60	120	6
12	1	40	60	130	6
13	2	40	60	130	7
14	1	40	60	140	5
15	1	40	75	110	8
16	1	40	75	130	9
17	1	40	90	130	6

a) The residence time in each reactor stage was the same, i.e., one half the total residence time listed here.

b) Excess N_2F_4 is the amount fed over that theoretically required, expressed in percent, to saturate the double bonds of DEPECH.

c) Thermal stability of the product in cc/g/100 hr at 80°C measured after 200 hr.

CONFIDENTIAL

(C) Excess of N_2F_4

(C) From runs 1-3 it is indicated that a 20% excess of N_2F_4 is insufficient to produce a thermally stable product with a 90°C second stage reaction temperature. With a 40 or 150% excess of N_2F_4 equivalent products were obtained. Most of the remainder of the work was carried out using a 40% excess of N_2F_4 . For production runs a 50% excess of N_2F_4 was employed to provide an additional safeguard in case of temporary upsets in rates, and in practice it was found that use of this 50% excess resulted in the formation of no inferior product due to incomplete reaction.

(C) Residence Time

(C) From the results of runs 4-7 it is seen that a residence time between one and two hours is sufficient at 90°C second stage temperature. Forty minutes is apparently not sufficient time for completion of the reaction.

(C) Reaction Temperature

(C) For most of the current work the first stage temperature was kept at 60°C for these reasons: (1) 60°C is about the lowest temperature at which the difluoramination reaction begins; therefore the likelihood of a dangerous runaway reaction would be diminished by working at this temperature; (2) more N_2F_4 can be dissolved in the reaction medium the lower its temperature; if the temperature exceeded the bubble point the evolved gas would displace liquid and therefore reduce the residence time.

(C) Runs 8-14 demonstrate the influence on thermal stability of second stage reactor temperature. Second stage temperature in excess of 90°C may be of benefit and definitely is not harmful. To assure consistent completion of reaction it would be expected that the best temperature would be the highest one which did not begin to bring about side reactions. Apparently a residence time of one hour at these second stage temperatures, as judged by runs 10 vs 9 and 13 vs 12, was neither beneficial nor harmful from the product property point of view; however the shorter residence time would be preferable from the point of view of hourly production. Second stage temperatures in excess of 140°C were not investigated; however those products prepared at 140°C demonstrated good thermal stability.

(C) Samples obtained from the first stage of the reactor were analyzed for NF_2 content and gave the results shown in Table 11. From these results

(C) Table 11. RATE OF DIFLUORAMINATION
OF DEPECH AT 60°C

<u>Residence Time, hr</u>	<u>NF_2 Content, %</u>	<u>Reaction, %</u>
0.5	39.0	46
1.0	47.8	66

CONFIDENTIAL

it was estimated that at 60°C the half life was about 37 minutes and the rate constant was 0.019 min^{-1} . As may be seen from runs 15 to 17 no significant improvement in product quality was observed by increasing the first stage temperature to 75 or 90°C. Therefore all further work was carried out with a first stage temperature of 60°C for reasons outlined above.

(C) DEPECH Concentration

(C) Most preparations carried out in the continuous reactor employed as feed an 11%w solution of DEPECH in acetone. At higher concentrations of DEPECH (16.5%w) some difficulties have been encountered occasionally due to the presence of gel particles in the feed vessel. Different batches of DEPECH have shown varying tendencies to form gels. No further work was carried out at higher feed concentrations. Runs have been carried out at a 5%w DEPECH concentration, but no improved product properties were observed.

(C) Pressure

(C) Initial runs were made at 300 psig, however the pressure was soon raised to 400 psig to prevent the possibility of gas bubble formation in the system as the temperature of the first and/or second stages was raised. No significant further increase in pressure could be examined with the current facilities since N_2F_4 liquifies at ambient temperatures at about 440 psig.

(C) Solvent

(C) All preparations in the continuous system have been carried out in acetone solution. Earlier work in the batch system indicated that the use of only 30%w methylene chloride in acetone served to degrade the PREP and produce low molecular weight byproducts. Therefore no chlorinated hydrocarbons have been used in the continuous system in spite of the greater solubility of DEPECH and N_2F_4 in these solvents.

(C) DEPECH Feed Solution Quality

(C) At one point in these studies all freshly prepared PBEP samples suddenly evidenced an absorption band at 4.47μ in the infrared spectrum, a region rather specific to the nitrile group. Analysis for fluorine and nitrogen of a sample possessing this absorption band gave results which could be accounted for if it was assumed that 10% of the NF_2 groups had been dehydrofluorinated to nitrile groups. Since presumably only the primary NF_2 groups could be dehydrofluorinated this would indicate that 20% of these groups had so reacted. In an effort to ascertain the cause for this sudden product change, PBEP samples were contacted with various corrosion products of the reactor system; however, no change in their IR absorption spectrum was effected by this treatment. The source of this problem was finally traced to the DEPECH feed which was in use at that time. When freshly prepared it had given a standard quality PBEP, but during inadvertent exposure to air for 6 to 8 weeks a reaction had apparently taken place which was responsible for the appearance of the nitrile group in the product. It was also shown with a different batch of DEPECH that storage under anaerobic conditions maintained

CONFIDENTIAL

its quality but storage with access to air developed in it also the propensity to produce nitrile groups in PBEP derived from it. Treatment of another sample of good DEPECH with oxygen or exposure to air for a considerable period of time did not cause it to develop the tendency to produce nitrile in the difluoramination reaction. It is inferred from this work that with certain samples of DEPECH at least exposure to oxygen can cause reactions to take place which may lead to PBEP of inferior quality.

(C) On one other occasion after having prepared high quality product for several days the product suddenly became dark in color, evolved HF, showed spurious peaks in the IR spectrum at 6.6 and 5.85 μ , and attacked the salt crystals used to support the film used for IR measurements. The cause of the problem was finally traced to the use of a new source of acetone solvent which was found to contain 0.36% water, higher by a factor of three than the water content of the acetone in use previously. Replacement of this wet solvent with acetone of standard dryness (0.1% water) resulted in the immediate return to the standard quality PBEP production. It is of interest to note that upon workup in the standard manner the spurious peaks in the IR disappeared and an apparently normal product resulted.

(C) Since the presence of a rather small amount of water in the acetone solvent had produced a rather large effect on the effluent product stream it was decided to evaluate completely dry acetone as a solvent for the reaction. Acetone which was dried over 13-X Linde molecular sieves and carefully fractionated through a 36-inch spinning band column was used as solvent in a batch PBEP preparation and afforded a product indistinguishable from the usual one in any of its properties.

(C) Sample Preparation

(C) To satisfy the needs of a number of Air Force contractors a series of 12 to 16 hour continuous PBEP preparations were carried out and the products combined into a forty-pound composite. The conditions employed are outlined in Table 12.

Table 12. CONDITIONS FOR PBEP PRODUCTION RUN

PBEP Production Rate	0.25 lb/hr
Solvent	acetone
DEPECH Feed Concentration	11%
Excess N_2F_4	50%
Residence Time	1 hr
First Stage Reactor Temperature	60°C
Second Stage Reactor Temperature	110°C
Pressure	400 psig
Method of Workup	Podbielniak extractor; pass over molecular sieve and silica gel beds.

CONFIDENTIAL

(C) Equipment performed satisfactorily and in line with expectations. Occasional plugging developed at the point where N_2F_4 and DEPECH/acetone solution were mixed. Redesign of this region to decrease points of stagnation served to essentially eliminate this problem. The final composite of PBEP had the properties shown in Table 13. These values are comparable to those obtained on PBEP samples prepared by the batch process with the possible exception that the molecular weight is higher by 300-400 units.

(C) Table 13. CHARACTERIZATION OF SOLVENT-FREE PRODUCTION SAMPLE

Sample No.	10001-186
C, %	24.5
H, %	3.5
N, %	15.8
F, %	40.5
NF ₂ , % (basis N)	58.7
F/N Ratio	1.89
OH, eq/100 g	0.045
OH Functionality	1.75
Molecular Weight	3900
Thermal Stability at 80°C, cc/g/100 hr	5.2
NCO Equivalent, eq/100 g	0.070

A sample of the composite was cured in the nonenergetic formulations shown below, Table 14. These tensile and elongation values compare favorably with similar data obtained on batch PBEP.

(C) Table 14. RESULTS OF CURING STUDIES

Properties	Formulation 1, %W	Formulation 2, %W
PBEP	27.81	27.52
Dibutyl Phthalate	22.57	22.33
Tolylene Diisocyanate	3.23	3.95
Glycerine	0.56 (2 phr)	0.83 (3 phr)
Dibutyltin Diacetate	0.50	0.50
Ammonium Sulfate	45.31	44.87
Tensile (max), psi	52.7	78.0
Elongation, %	47.8	30.2

CONFIDENTIAL

DOCUMENT CONTROL DATA - R&D	
(Security classification of title, body of abstract and indexing annotation must be entered when the report is classified)	
1 ORIGINATING ACTIVITY (Corporate author) Shell International Chemical Company, Ltd. Oil Company, London, England	2a REPORT SECURITY CLASSIFICATION CONFIDENTIAL 2b GROUP
3 REPORT TITLE ENERGETIC POLYMERIZATION	
4 DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Technical Report, AFOSR-TR-66-184, 1966	
5 AUTHOR(S) (Last name, first name, initials) Hunter, L., Ryder, R. H.	
6 REPORT DATE October 1966	7a TOTAL NO OF PAGES 69 7b NO OF REFS
8a CONTRACT OR GRANT NO AF 64(611)-1164 b PROJECT NO 14c c FICR 625147 d	9a ORIGINATOR'S REPORT NUMBER(S) 1-14075 9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFRPL-TR-66-184
10 AVAILABILITY LIMITATION NOTICES In addition to security requirements which must be met, this document is subject to special export control and such transmittal to foreign governments or foreign nationals may be made only with prior approval of AFRL (RPR-STINFO), Edwards, California 93523	
11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY Air Force Rocket Propulsion Laboratory Research and Tech. Div., Edwards, Calif. Air Force Systems Command, U.S.A.F.
13 ABSTRACT (C) PBEP has been fractionated by solvent gradient elution from a Chromosorb W-packed column. Molecular weight distribution of the polymer has been determined and the fractions evaluated through exhaustive analyses and small scale cure studies. PBEP has been also separated into two fractions by extraction with carbon tetrachloride. The properties of the fractions have been compared and the more promising higher molecular weight fraction extensively evaluated. (C) Fractionating of the polymer at an earlier stage in the synthesis has been investigated. Polyepichlorohydrin (PECH) has been separated into two fractions and the higher molecular weight fraction evaluated by conversion to PBEP. (C) The carbon treatment of PBEP has produced promising improvements in the thermal stability of the polymer and in reducing the deactivating effect of the latter on the cure catalyst. (C) Small scale curing studies have compared the reaction of tolylene diisocyanate (TDI) with PBEP and other ingredients in the cure system. Deactivation of the cure catalyst by PBEP has been demonstrated and promising leads towards prevention have been investigated. (C) The stability of PBEP in solution has been investigated at high and low temperatures for extended periods. (C) Large scale batch preparations of polyepichlorohydrin (PECH) and dehydrochlorinated PECH (DEPECH) have been carried out. A two-stage continuous reactor system for difluoramination of DEPECH has been constructed and operated for the production of experimental quantities of PBEP for evaluation by propellant contractors. A brief investigation of the process variables has been carried out to determine near optimum conditions for the continuous system.	

DD FORM 1473
1 JAN 64

CONFIDENTIAL

UNCLASSIFIED

14. KEY WORDS

High Energy Binders
Solid Propellants
PBEP

AFRPL-TR-68-184

-43-

UNCLASSIFIED